PROTECTIVE FILMS ON METALS

A SERIES OF MONOGRAPHS ON APPLIED CHEMISTRY.

Under the Editorship of E. HOWARD TRIPP, Ph.D.

Other volumes are in course of preparation, and detailed particulars will be sent from time to time to anyone sending a request.

PROTECTIVE FILMS
ON METALS

BY

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BEING VOLUME FIVE OF A SERIES OF
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EDITORIAL PREFACE.

IN these days of intensive and extensive research, every worker in science or its applications knows how rapidly the contents of text-books and encyclopædias become out of date ; and those who wish to see new work published know the difficulties which abnormal taxation and high labour costs offer to the realisation of their desire. The one obvious solution of the problem is the publication of monographs that would focus attention upon recent work, or upon new aspects of old work, and upon their theoretical implications. Such books are usually written by experts for other experts in related fields of science, or for the well-educated layman whose thirst for new knowledge has not been quenched by the more sensuous outpourings of the ephemeral press.

It is interesting at times to speculate upon what aspects of our civilisation the future historian will select as the most characteristic of our time. Scientific discoveries and their application to human welfare, we may be sure, will find a place ; and to these many will add the growth of our sense of "values." The value of new work in science varies greatly : the golden grain is always accompanied by chaff, and there is no precious ore without country rock. Owing to the difficulty of assessing the value of work at the time of its production, we find that our scientific periodicals stand in danger of being swamped by the mass of second- and third-rate material that

is thought to be worth publishing, but which posterity will decree would have been better left in manuscript form. It is the first duty of the monograph writer to estimate the value, either actual or potential, of recent work upon the subject of which he writes : he must pick out the plums to save others from the indigestion that follows eating the whole pie. Further, in addition to being accurate, his work must be presented in a form that is both assimilable and attractive ; in other words, he must show that lucid exposition can be achieved by the use of few words, if they are rightly chosen, and that attractive presentation is attained rather by clear thinking than by superficial display.

The present series of monographs has been designed with these objects and ideals in view. The task which the authors have been set is no easy one ; so that should performance occasionally fall short of intention, the critical reader is asked to echo the words of Goethe that " higher aims, even if un-fulfilled, are in themselves more valuable than lower aims quite attained."

<div align="right">E. HOWARD TRIPP.</div>

AUTHOR'S PREFACE.

AT a time when Economy has become almost a world-religion, when schemes for utilising waste products are being developed to their fullest extent, when it has come to be realised not only industrially, but politically, that prevention is better than cure, and when the annual loss to the world through the corrosion of metals is estimated as something like £500,000,000, scientific research aiming at the preservation of metal structures is of more than usual interest and importance.

With the increase in the use of different metals in both the structural parts and ornamentation of buildings and in other situations involving exposure to atmospheric corrosion, in chemical plant, aircraft, and numerous other branches of industry, the need of a proper understanding of the principles of the protection of metals against corrosion of all types has become greater in proportion.

Of recent years much research has been conducted on the properties and isolation of thin films which form spontaneously on metals under certain conditions and protect them from further chemical attack. This work provides an excellent example of the ultimate economic and practical value of experiments conducted in the academic laboratory.

The present book describes work on the examination of both natural and artificial protective films, and discusses problems of passivity and anodic films and their practical

applications, including stainless steel and decorative oxidised finishes. In a rough way the book is in two parts, Chapters VII. to XII. being devoted mainly to the practical side, including accounts of the protection of metals by metallic films (applied by hot-dipping, electro-deposition, spraying, cementation, etc.). The growth of the food-canning industry in this country has made desirable the inclusion of a brief account of the protective properties of the tin-plate container.

A chapter is included on the corrosion of metals, in so far as it has a bearing on problems of protection.

In compiling this book I am indebted to many friends who have sent me copies of their publications, but particularly to Mr. U. R. Evans, M.A., of Cambridge ; Dr. G. D. Bengough and Dr. W. H. J. Vernon, of Teddington ; and Professor W. J. Müller, of Vienna, with whom I have had the privilege of discussing those portions of the book which refer to their work.

My thanks are also due to Dr. E. H. Tripp, the Editor of this series, for his valuable suggestions, to the Council of the Chemical Society for permission to reproduce portions of my papers presented to the Society, and to the Council of the Faraday Society for permission to reproduce Fig. 13.

E. S. H.

October, 1931

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CHAPTER I.

INTRODUCTION.

IT happens not infrequently in the history of Science that a single decade witnesses independent activities of researchers in different parts of the world, directed towards the same or closely similar subjects. A feature of recent years is the recognition of the part played by thin films in protecting metals from corrosion. It is interesting to note that almost a hundred years ago Faraday evolved the idea of a protective oxide film to explain the chemical passivity of iron towards concentrated nitric acid, but the last ten years have seen the proof that such films actually exist and that the knowledge gained from them can be utilised to advantage.

From Faraday's pure guess, the protective oxide film has passed through the stage of a well-backed hypothesis to a demonstrable fact, for films have now been isolated and rendered visible in practically all the known cases of passivity. But passivity is only one aspect of film formation and there are other films besides those of oxide. Nevertheless, passivity is a natural and spontaneous protection against the attacking chemical agent, and most artificial improvements are best made by first investigating thoroughly the natural process. The stainless steels are automatically kept in a passive condition by the action of the air.

PROTECTIVE FILMS ON METALS

Indeed, the study of naturally acquired protective films of oxide is an illustration of the practical and economic advantages of researches which are conducted in the first instance often from purely academic interest. To give an example, every one has suspected for a long time that aluminium, a remarkably reactive metal under certain conditions, owes its chemical stability to the possession of a thin film of oxide acquired from the atmosphere, which serves to protect it from corrosive influences. It is possible to strengthen this invisible film by making the aluminium the anode of an electrolytic cell containing an oxidising solution, and this process is now used all over the world for the protection of aluminium from corrosion.

Another line of investigation has been the study of anodic processes, where it has long been known that at high current densities anodes of certain metals tend to become passive and cease to dissolve, or go into solution relatively slowly and perhaps in a different ionic state. There is now almost complete agreement that these processes also are due to the formation of protective films, and the knowledge thus acquired leads to at least two important practical applications. It suggests means by which metals may be protected artificially, and it also indicates the means of overcoming the troublesome phenomenon of passivation in the electro-refining and electro-plating industries. Such protective films are not necessarily of oxide and many examples of films of other compounds which may be protective in certain circumstances will be found in the following pages.

A feature of special interest and often of surprise is the extreme thinness of many protective films, which in some cases are believed to be of only one or two molecular layers.

INTRODUCTION

At first sight it would seem that such thin films could have no practical significance ; nevertheless, the chief difference in the rust-resisting properties of stainless and ordinary steels is related directly to the properties of this invisible film. Actually, the protective film on stainless steel is thinner than that on ordinary steel. The reason is that an efficiently protective film stifles its own growth, and the fact that a film grows to any considerable thickness indicates that its protective effect is imperfect. So far as spontaneously acquired films are concerned, the ideally protective film is one which ceases to grow when it attains a thickness of one molecule.

The study of anodic passivation has definitely shown that in many cases the anode may acquire two separate films, the first of which is visible and non-protective and the second invisible and protective. It is necessary to emphasise that *the protective power of a film is a relative term*, depending on all the existing conditions, and a film which is protective in some circumstances may be almost or quite useless in another set of circumstances. In any case, there are all intermediate degrees of protection from that offered by a spongy mass, which merely hinders diffusion of reactants and products, to that afforded by a unimolecular layer of a practically insoluble compound.

In spite of the isolation of many spontaneously acquired protective films, it is difficult in most cases to obtain reliable information of their chemical composition or physical structure. It is possible that the chemical composition of a unimolecular film cannot always be related to the chemical compounds recognised in the massive state, for such films may be regarded as two-dimensional compounds. X-ray methods of investigation can reveal little or nothing of the physical

structure of thin films on a crystalline background, and up to the present the thinnest films have eluded the newer method of electron-diffraction. Recently, the condition of matter in the film state has become a subject of enquiry, and A. V. Blom (*Kolloid-Z.*, 1931, **54,** 210) has advanced the conception of a film as a particular state of matter intermediate in properties between dispersoids and compact solid matter. Sir W. Hardy (*Phil. Trans.*, 1931, **A., 230,** 1) considers films as a fourth state of matter characterised by the sharing of the energy with the adjacent phases.

As a rule it is not necessary, however, to ascribe protective properties of a film to any peculiar state of the matter, for the compound concerned generally protects the underlying metal only under conditions where the massive material would be stable. An example is the former controversy that a film of metallic oxide can scarcely be expected to protect a metal from an acid solution. Actually, the three metals which are most readily rendered passive (iron, chromium, and aluminium) are well known to give oxides which when freshly ignited are practically insoluble in acids. When the conditions are such that these oxides are readily soluble the metals immediately regain their activity.

Sulphide and other films of relatively poor protective value are often applied to metals mainly for the purpose of decoration. They are generally sufficiently protective for indoor exposure when incorporated with oil or coated with shellac or similar material. Apart from their decorative value, these films provide an excellent groundwork for a subsequent coat of paint, lacquer, or enamel, for they act as a bond between the otherwise dissimilar phases and minimise the risk of peeling or flaking of the outer layer.

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In practice, the most desirable protective coating for a given metal depends on numerous factors. Besides economic and æsthetic considerations the chemical environment and mechanical requirements are important. Machine parts which have to fit must be coated in such a way as not to increase the thickness sensibly, parts which have to undergo fabrication after coating or which suffer deformation in service must have a coating which does not crack or peel on bending, and parts subject to wear must be coated with material which is resistant to abrasion.

Films of the oxide type, whilst fulfilling some of these conditions, are not resistant to wear, and unless they are automatically kept in repair by the action of the atmosphere must have a limited use. That is the advantage of the stainless steels ; atmospheric oxidation keeps constantly in repair the exceedingly thin, highly protective film. Chromium and aluminium come in the same category. Naturally acquired protective films are ideal so long as they can be kept in repair automatically under the conditions of use.

On the other hand, the metals offer a large range of mechanical properties desirable in a protective coating and present an artificial source of protective metallic films. The protection of metals by metallic films involves several large industries. Special interest is attached to the protection of iron, and two kinds of protection may be afforded by metallic films. When the protecting metal is less noble than the base metal, as in coatings of zinc or cadmium on iron, the protection is partly electrochemical. In the presence of a thin film of electrolyte solution the zinc becomes the anode and corrodes, whilst the iron becomes the cathode and parts of exposed iron in close proximity to the zinc are free from attack. The presence

of perforations in a protective metallic film of this type, although very undesirable, is not so serious a matter, because the protective layer corrodes preferentially.

When the protecting metal is more noble than the base metal, for example, when iron is coated with nickel or copper, the electrochemical effect is reversed and the protection afforded is mechanical. Such metallic films act by excluding corrosive agents from the base metal and are effective only so long as they completely cover the surface. A discontinuous film is generally worse than the total absence of a film. Exposed surfaces of iron in a copper-coated iron sheet will become anodic to the adjacent copper and corrode more rapidly than if the whole surface of the specimen were iron. Where small areas are left unprotected, partial or complete perforation of the material may occur eventually, and severe localised corrosion is more objectionable than the same amount of corrosion evenly distributed over the entire surface. In certain instances the usual electrochemical relations of the base metal and the protecting metal may be reversed, as has been demonstrated in the corrosion of the tin-plate food container.

Metallic films are usually applied by hot-dipping, electrodeposition, spraying, cementation, or mechanical means, and the structure of the coating is different in each case. The mechanical properties of the coating may not be identical with those of the metal applied, for in some cases the formation of an alloy of the two metals is an essential constituent of the coat and may be so brittle that subsequent deformation of the work must be avoided. In addition, the method of application of the protective metal may have an important influence on the mechanical properties of the base metal. For example, the hot-dipping process may produce some

annealing of the base metal and is not suitable, therefore, for coating springs. Spraying has the advantage that large structures may be treated *in situ*.

Other artificially applied protective films consist of compositions such as paints, varnishes, lacquers, and enamels. These act partly like a layer of grease or oil by excluding corrosive agents from the surface of the metal, but in certain instances have a more specific action. For example, oxidising pigments, such as red lead and certain chromates, tend to maintain a passive film of oxide at the surface of iron work, whilst aluminium and zinc paints act in a sacrificial way.

CHAPTER II.

THE MECHANISM OF CORROSION.

THE application of a remedy is best understood by first en-
quiring into the causes of the evil, and the protection of metals
against corrosion can be on only an empirical basis unless the
fundamental principles of corrosion are understood. This sub-
ject has been treated in a very admirable way by U. R. Evans
("Corrosion of Metals," Arnold & Co., 2nd Edn., 1926),
who has given a detailed account of the views held at the present
time. It is proposed to discuss here certain features of these
views, in so far as they affect the problem of the protection
of metals.

Most chemists would agree that in the main there are two
ways in which corrosion can occur. Embracing for the moment
all reactions in which metals are transformed into their com-
pounds under the term corrosion, it may be said that these
reactions take place either by direct chemical attack or by
electrochemical action. Examples of direct chemical action
are provided by the reactions of ordinarily dried chlorine,
hydrogen sulphide, and other gases on dry metals. The
course and extent of the reaction in such a case depends mainly
on the physical properties of the product, provided that the
energy changes involved are such that the chemical reaction
takes place spontaneously. If the product is liquid or gaseous
at the temperature of the reaction it will be removed con-
tinuously and the reaction may continue until the reactants

are used up. If the product is solid, it will remain where it is formed and will hinder more or less the attack of the corrosive agent on the metal. Incidentally, this principle has an interesting application in the recovery of tin from scrap tinned iron, for when dry chlorine is led over the material the tin reacts continuously to form stannic chloride, whilst at the temperature used the iron merely acquires a film of ferric chloride.

These solid films may have different degrees of porosity. When the film is porous it allows the attacking gas to penetrate it and reach the underlying metal, so that corrosion continues, but at a slower rate than if the film were absent. Meanwhile, the film is increasing all the time in thickness and may eventually flake off in parts. Such a film has poor protective properties. The fact that a film reaches a considerable thickness is in itself sufficient to indicate a porous structure, for a protective film prevents its own growth automatically. On the other hand, when the film is dense and impervious to the attacking gas it isolates the underlying metal, and a film so thin as to be invisible may entirely prevent further attack. A spontaneously formed protective film will always be thin.

In the course of atmospheric corrosion, metals which are exposed to industrial fumes may suffer attack by gases such as those mentioned, but on the whole this type of action constitutes only a very small fraction of the corrosion of metals. This is particularly the case so far as the direct action of oxygen is concerned. Even on the reactive metals dry oxygen has very little action ; iron preserved in pure, dry oxygen is quite free from rust. Chemical action certainly ensues, but the product is a solid oxide, which coats the underlying metal and shields it from further attack. At more elevated tempera-

tures the oxide film may crack and cease to preserve its protective properties, or it may become permeable to oxygen, and then a thick loose scale will be formed and eventually the whole of the metal may become oxidised ; but that does not happen at the ordinary temperature with ordinary commercial metals. Other metals, such as the alkali and alkaline-earth metals, have a considerable vapour pressure at moderately elevated temperatures and direct reaction between the vapour of the metal and oxygen ensues on heating ; the heat of combustion melts and vaporises the remaining metal, so that these metals burn vigorously in the air when given a preliminary heating. At the ordinary temperature, however, oxidation by dry oxygen is confined to a surface layer. When the metal is nearly all surface, that is to say, when it is finely divided, it may be completely oxidised. Pyrophoric iron and other metal powders have been described, and the ready inflammability of magnesium powder is well known. Powdered aluminium burns quite easily, although when the massive metal is heated in air or oxygen it merely acquires a superficial film of oxide and there the reaction stops.

Electrochemical Corrosion.

It is usual to distinguish between atmospheric corrosion and corrosion in aqueous solutions, but whilst for practical purposes the distinction is very convenient it does not appear to have a logical basis. In the ordinary way atmospheric corrosion occurs in the presence of a film of water, and the presence of this film is a factor the importance of which cannot be over-estimated. A method of preventing the ordinary rusting of iron is always to keep the temperature of the specimen well above the dew-point, so that liquid water does not

condense on it. Corrosion is initiated, however, before 100 per cent. relative humidity is reached. Actually, the thinnest film of water can be removed only by heating the specimen fairly strongly, but the electrical conductivity of such tenuous films is probably so small that they have no important influence. Metallic objects exposed out-of-doors are open to the condensation of relatively thick films of water, even if they are sheltered from the rain, and when the surface has once become coated with a porous skin of corrosion products the skin aids the retention of water.

To the writer it seems more logical to differentiate between corrosion occurring in the presence or in the absence of an electrolyte, for to a large extent atmospheric corrosion takes place in the presence of a film of electrolyte. Where no electrolyte is present the corrosion must be attributed to direct chemical action, but when an electrolyte is present the corrosion may be wholly or partly electrochemical. In any case, in actual practice both types of attack will often occur simultaneously. For example, hydrogen sulphide may be supposed to have a direct chemical action on a metal, but when the metal is covered with a film of water an electrochemical effect cannot be excluded. On the other hand, an impure specimen of zinc may be supposed to dissolve in dilute sulphuric acid through the setting up of an electrolytic couple between the anodic zinc and the cathodic impurities, but in many cases of metallic dissolution it has been shown that the change is not so simple and that ordinary chemical forces are involved. In some cases it seems that the fundamental reactions are not ionic, the metal reacting directly with the molecules of the acid. It is realised that a distinction between chemical and electrochemical phenomena becomes very

difficult and almost meaningless when applied to molecules and ions, but nevertheless in the scale of ordinary experience the terms do have a definite significance.

Electrode Potentials.

The theory of electromotive force is discussed in text-books of electrochemistry, and it is proposed to give here only the briefest outline of the way in which an electrolytic cell is set up. According to the well-known classical theory of Nernst, each metal has a definite *solution pressure*, which is a measure of the tendency of the metal to pass into aqueous solution in the form of ions. This solution pressure is opposed by the osmotic pressure of the metal ions, which tends to drive them out of solution, depositing them on the metal. When a metal is immersed in an aqueous solution of one of its salts the solution pressure of the metal (P) tends to increase the number of ions in solution and the osmotic pressure of the ions (p) tends to decrease the number of ions. The result is illustrated by Fig. 1 and depends on whether P is greater than, equal to, or less than p. With the " reactive " metals, such as zinc, P is greater than p, positively charged zinc ions go into solution, and the metal acquires a negative charge (Fig. 1, *a*). When the solution and osmotic pressures are equal (*b*), no ionic change occurs and no electropotential is developed. When P is less than p (*c*), as in the case of copper and the " nobler " metals in solutions of their salts, ions of the metal are deposited, giving a positive charge to the electrode, whilst the solution in the vicinity is negatively charged by the corresponding anions. The surface of the electrode is thus the seat of an electrical double layer.

As shown in the next section, the potential developed is

a quite definite characteristic for a given metal and it is capable
of being measured. To make the measurement, the half-
cell constituting the metal electrode in a solution of its salt
is combined by means of a liquid junction with a standard
half-cell, which consists usually of a hydrogen electrode or
a calomel electrode. The hydrogen electrode is really
blackened platinum kept saturated with hydrogen at atmo-
spheric pressure and immersed in an acid solution of normal
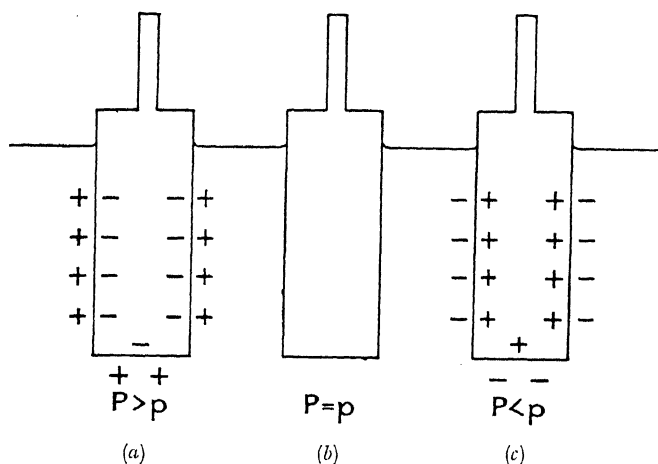
FIG. 1.—Solution pressure of metals.

concentration with respect to hydrogen ions. The calomel
electrode consists of a layer of mercury covered with a paste
of mercurous chloride in a solution of decinormal, normal,
or saturated potassium chloride. The combination of the
electrode to be measured with the standard electrode forms
a complete cell, the total potential difference of which can be
measured by a potentiometric method. The values obtained
in this way are not absolute, although methods have been
proposed for determining absolute potentials, but are relative

to the standard electrode and are therefore strictly comparable. This renders it necessary to state the standard of reference when discussing electrode potentials, and it is most customary to refer such potentials to hydrogen as zero. Except where otherwise stated, this system will be used in the present book. A note on the convention as to sign is in place here, as in the past there has been a certain amount of confusion. The convention recommended by most scientific societies is to call the more reactive metals (sodium, zinc, etc.) negative and the nobler metals (platinum, copper, etc.) positive, and this system will be followed.

Theoretically, the potential of a metal immersed in a solution of one of its salts is given by the expression

$$E = \frac{RT}{nF} \log_e \frac{P}{p}, \qquad . \qquad . \qquad . \quad (1)$$

where R is the gas constant, T the absolute temperature, n the valency of the metal ions, F is 1 Faraday, or the number of coulombs associated with the dissolution or deposition of 1 gram-equivalent of metal, P is the solution pressure of the metal, and p the osmotic pressure of the metal ions. Putting R (1·99 cal.) into electrical units by multiplying by Joule's factor 4·183, putting $F = 96,540$ and multiplying the expression by 2·3026 in order to convert natural logarithms to ordinary logarithms to base 10 the expression simplifies to

$$E = \frac{0·0001983 \; T}{n} . \log_{10} \frac{P}{p} . \qquad . \qquad . \quad (2)$$

The osmotic pressure varies with the concentration of the solution and the potential of an electrode will therefore vary with the ionic concentration of the salt solution in which it is immersed. By applying the gas laws to dilute solutions

we may replace the pressures P and p by the ionic concentrations C and c and re-write the expression in the form

$$E = \frac{0 \cdot 000198 \, T}{n} \, . \, \log_{10} \frac{C}{c}, \qquad . \qquad . \qquad (3)$$

where c is the concentration of metal ions in the neighbourhood of the electrode.

Suppose the metal to be immersed in a $1 \cdot 0$ M solution of its ions, then $c = 1$ and $\log_{10} c = 0$, so that for a normal solution the equation becomes

$$E_0 = 0 \cdot 000198 \, T/n \, . \, \log_{10} C \qquad . \qquad . \qquad (4)$$

The argument is made clearer by re-writing equation (3) in the form

$$E = 0 \cdot 000198 \, T/n \, . \, \log_{10} C - 0 \cdot 000198 \, T/n \, . \, \log_{10} c.$$

Thus, for any other concentration the electrode potential is given by the formula

$$E = E_0 - 0 \cdot 000198 \, T/n \, . \, \log_{10} c,$$

in which E_0 is the *normal electrode potential.*

To give an idea of the magnitude of the variation of potential with concentration of the solution, it may be stated that at $18°$ C. whenever the ionic concentration is diluted to one-tenth of its former value the potential is displaced in the negative direction by about $0 \cdot 058$ volt for a univalent ion, $0 \cdot 029$ volt for a bivalent ion, and $0 \cdot 019$ volt for a tervalent ion.

In passing, it may be noted that it is possible to have an appreciable difference of potential between two pieces of the same metal immersed in solutions of the same salt at different concentrations. Such an arrangement is called a *concentration cell.*

The Electrochemical Series.

In the following table are given values of the normal electrode potentials of a number of common metals, arranged in order, and constituting what is known as the *electrochemical series* :—

<div align="center">NORMAL POTENTIALS.</div>

Metal.	Volts.	Metal.	Volts.
Platinum	+ 0·86	Cobalt	0·23
Silver	+ 0·7987	Iron (ferrous)	0·34
Mercury (ous)	+ 0·7928	Cadmium	0·420
Copper	+ 0·3469	Zinc	0·770
Hydrogen	0·000	Aluminium	1·337
Lead	— 0·132	Magnesium	1·8
Tin	— 0·146	Sodium	2·715
Nickel	— 0·20	Potassium	2·925

The chief features to be observed are that the reactive metals fall at the lower end of the series, whilst the nobler metals are the first members of the series. Hydrogen is taken as an arbitrary zero, all the values being expressed on the hydrogen scale. The values vary slightly with the condition of the metal ; for example, cold-working is said to shift the potential slightly in the negative direction.

In general, any metal in the series will displace from their salt solutions metals which precede it in the series. Thus, magnesium reduces iron from ferrous solutions, iron turns out copper from cupric solutions, and copper in turn deposits silver from a solution of silver nitrate. The further removed are the metals in the series, the more readily does this electrochemical replacement occur. The behaviour of hydrogen in this respect is interesting and is particularly important in

the study of the corrosion of metals in aqueous media. Metals which precede hydrogen in the series will not normally displace hydrogen from acids, whilst metals which follow, such as tin, iron, zinc, and magnesium, will do so with increasing ease. Indeed, the alkali metals, at the extreme lower end of the series, will displace hydrogen even from water, where the concentration of hydrogen ions is exceedingly low. At the same time, it is necessary to bear in mind that the potentials given refer to metals in contact with normal solutions of their ions and, as already shown, this potential can be varied considerably by reducing the concentration of metal ions to a very small value. Under special conditions, therefore, the behaviour of the metals may be different. Thus, copper does not normally displace hydrogen from solutions of acids because the potential of copper in contact with the ionised cupric salt solution which would be formed is higher (more positive) than that of the hydrogen produced in contact with the solution of hydrogen ions. On the other hand, when copper is warmed with concentrated hydrochloric acid it dissolves as the complex anion $CuCl_2'$, which is in equilibrium with an exceedingly small quantity of copper ions, and evolution of hydrogen therefore occurs in this reaction. For the same reason, when two metals have very close normal electrode potentials they may mutually displace each other from solution ; thus tin precipitates lead from a solution of a lead salt, whilst when metallic lead is placed in a solution of a tin salt metallic tin is formed and lead goes into solution.

Electrolytic Couples.

When two metals having different electrode potentials are placed in an electrolyte solution, a difference of potential

is set up. This potential difference is the seat of an *electromotive force*, and by connecting the two metals externally an electric current can be obtained. The magnitude of the electromotive force increases as the position of the two metals is more remote in the electrochemical series. The two dissimilar metals in the electrolyte are a potential source of energy and constitute an electrolytic couple.
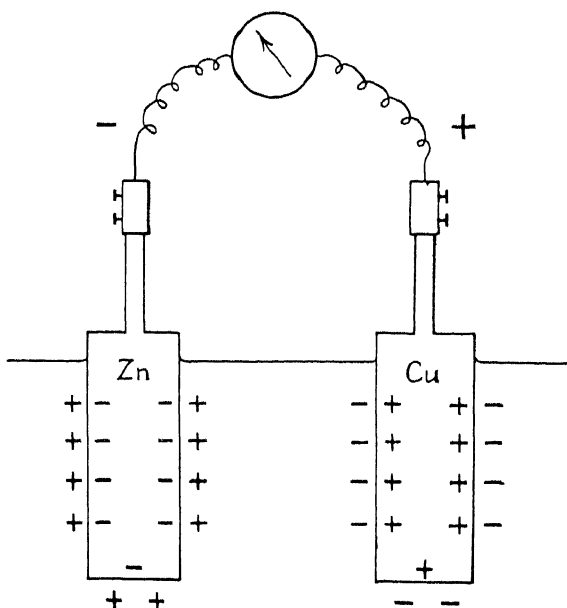
FIG. 2.—The zinc-copper couple.

Fig. 2 is an illustration of such a system. When zinc is immersed in dilute sulphuric acid it becomes negatively charged, positive zinc ions going into solution. On the other hand, copper becomes positively charged when immersed in the same solution. When the two metals are joined externally by a wire, as shown in the diagram, a current flows outside the cell from the positive copper pole to the negative zinc

pole and can be observed by the deflection of the needle of the ammeter placed in the circuit. (The current is always regarded as flowing from the positive to the negative pole, although the negative electrons actually move in the opposite direction.) Some of the zinc dissolves to form zinc sulphate, and an equivalent quantity of hydrogen is liberated at the surface of the copper. When an external current is applied the metal which dissolves is regarded as the positive pole and is called the *anode*, whilst the other electrode, at which hydrogen is evolved or metal is deposited, is negative and is termed the *cathode*. The apparent confusion of the terms " positive " and " negative " is due to the fact that the current flows in one direction (from copper to zinc) *outside* the cell and in the opposite direction (from zinc to copper) *inside* the cell, thus performing a complete cycle.

If the electromotive force of this cell is measured by shunting a voltmeter across the terminals, or by any other method, it will be found that momentarily it corresponds approximately with the difference in the normal electrode potentials of copper and zinc, but the potential rapidly falls to a much lower value ; the current registered falls to a low value in the same way. This is because when hydrogen collects on the copper electrode it soon transforms it into a hydrogen electrode, and the zinc-copper cell no longer exists as such. The cell is said to be *polarised*. A small residual current continues to flow because the hydrogen slowly diffuses away or is removed by other means.

If an oxidising agent, such as potassium dichromate or potassium permanganate, is also present, it will oxidise the hydrogen at the copper electrode and so remove it as fast as it is formed. The oxidising agent is called a *depolariser*, and

if efficient the current will flow continuously until all the zinc has dissolved. In the Leclanché cell the depolarising agent is powdered manganese dioxide, which can only dispose of the hydrogen slowly; the cell is useful only for intermittent work, therefore, such as is required of the electric bell. If used continuously it soon becomes polarised. Oxygen itself acts as a slow depolariser and may be regarded in this light in certain types of corrosion involving the slow production of hydrogen.

Short-Circuited Cells.

When zinc and a more noble metal are placed in *contact* with each other in an acid solution a short-circuited electrolytic cell is produced, the current passing directly from one metal to the other and back through the solution. In the case mentioned, the zinc becomes anodic and sends zinc ions into solution, whilst the copper becomes cathodic and hydrogen is freely evolved at its surface. Whether the current and the process of dissolution will be continuous depends not only on the presence of depolarising agents, but on the hydrogen-ion concentration and on the hydrogen overpotential of the more noble metal—a factor which will be discussed later.

A rough attempt to show how the current is disposed when a small piece of copper embedded in zinc is immersed in dilute sulphuric acid is made in Fig. 3. Since the electrical resistance of the electrolyte is greater than that of the metal, the current will tend to take the shortest path and will be more concentrated in the portion of zinc adjacent to the copper than in the distant portions of zinc. The corrosion will be relatively greater near the junction of the two metals. For the same reason, the relative areas of copper and zinc exposed

have an important influence; if the amount of zinc is small, there is a relatively large cathodic area from which hydrogen can be evolved or disposed of by other means, and all the
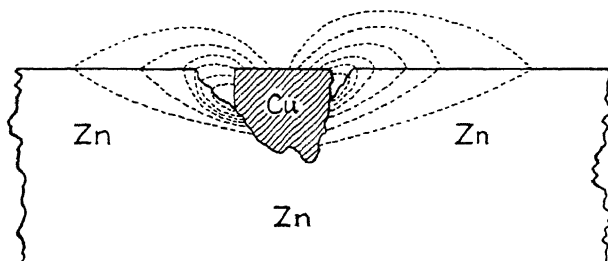
Fig. 3.—Short-circuited electrolytic cell.

attack is concentrated on a small area of zinc and the phenomenon of " pitting " occurs. This type of corrosion or dissolution is particularly likely to occur when a reactive metal has been coated imperfectly with a nobler metal.

Hydrogen Overpotential.

The hydrogen electrode consists of platinised platinum saturated with hydrogen at atmospheric pressure and immersed in a solution of hydrogen ions. This electrode is thermodynamically reversible and represents an equilibrium condition in the sense that at a slightly higher potential hydrogen passes from the electrode into the ionic state, whilst at a slightly depressed potential more gaseous hydrogen is produced from ions in solution. This reversibility occurs, however, only when the surface is of platinum black. At all other surfaces, including bright platinum, the production of bubbles of hydrogen does not occur until the potential has become more negative than the equilibrium value. These systems are irreversible hydrogen electrodes.

The difference between the equilibrium potential at a reversible hydrogen electrode and the potential of hydrogen evolution at the surface of a given metal is termed the *hydrogen overpotential* or *overvoltage* of that metal. The overpotential is characteristic of the metal and, as the following table shows, varies considerably from one metal to another, being exceptionally high for mercury and zinc. These values are approximate, for the overvoltage varies somewhat with the physical nature of the surface of the cathode material; it is smaller on a rough surface than on a smooth surface, a fact which can be correlated with the facility with which bubbles or any new phase forms at a roughened surface.

HYDROGEN OVERPOTENTIAL.

Metal.	Volts.	Metal.	Volts.
Platinum (bright) .	0·01	Cadmium . . .	0·5
Gold . . .	0·02	Tin	0·5
Iron (in alkali) . .	0·05	Lead . . .	0·6
Silver . . .	0·1	Zinc . . .	0·7
Nickel . . .	0·15	Mercury . . .	0·8
Copper . . .	0·25		

Various theories have been proposed to explain hydrogen overpotential from the point of view of the formation of metallic hydrides, the catalytic effect of the metal on the union of hydrogen atoms to form molecules, solubility of hydrogen in the metal, the surface energy involved in the formation of a new phase, and other considerations. These are discussed in text-books of electrochemistry and need not be of further concern here, but it is important to bear in mind that hydrogen evolution can occur readily at some metallic surfaces, but

only with difficulty at others having a high hydrogen over-potential.

The Dissolution of Metals in Acids, Alkalis, and other Reagents.

By the dissolution of metals is understood corrosion where the products are soluble in the corrosive liquid. The present discussion will be limited to the dissolution of metals with evolution of hydrogen, and other types, such as the action of nitric acid on metals, will not be considered here.

The student's earliest introduction to Chemistry gives him the experience of producing hydrogen by dissolving a reactive metal such as zinc in dilute sulphuric or hydrochloric acid. Although regarded as a very simple and elementary chemical operation the mechanism of the change is probably complex, and is certainly not fully understood at the present time. Text-books of Inorganic Chemistry represent the reaction by the equation

$$Zn + H_2SO_4 = ZnSO_4 + H_2,$$
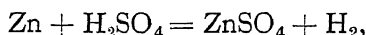
thereby neglecting the mechanism completely. Text-books of Electrochemistry represent the change in the form

$$Zn + 2H^{\cdot} = Zn^{\cdot\cdot} + H_2,$$
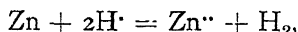
indicating a transference of electrons from zinc to hydrogen, whereby the zinc becomes ionised and an equivalent amount of hydrogen ions become discharged and join up to form molecules. The sulphate ion is left out of account, because it is there before the reaction in the form of sulphuric acid and after the reaction in the form of zinc sulphate. That the true process cannot be represented so simply is clear when it is pointed out that hydrogen-ion concentration is only one

of the factors determining the dissolution of the metal and that the influence of the anion is at least as important. Some metals which dissolve readily in hydrochloric acid scarcely dissolve in sulphuric acid of the same hydrogen-ion concentration. Although a fair amount of research has been conducted on the kinetics of the dissolution of metals, on the whole the light thrown on the process thereby is meagre and in certain aspects even contradictory. Special mention must be made of the valuable work of Centnerszwer and his collaborators in this field.

One of the most important and difficult problems is whether any direct chemical action takes place between metals and acids independently of electrochemical influences caused by the presence of impurities. Metals are exceedingly difficult to purify, and all ordinary metals will contain a certain amount of carbon or noble metal in their composition. When these impurities form a separate phase they act cathodically to the reactive metal (say zinc) on immersion in an acid solution, and short-circuited electrolytic cells are formed in the way described. There is little doubt that in the majority of cases this effect accounts for most of the dissolution. When the impurity forms a continuous and homogeneous phase with the metal, as in certain alloys, its presence may actually retard corrosion, hindering the passage of the attacking acid to the reactive metal. In such a case, slow dissolution of the reactive metal generally occurs and the impurity is eventually deposited at the surface as a separate phase and then the velocity of dissolution is increased by its electrochemical action.

Whether perfectly pure metals will dissolve in acids with the evolution of hydrogen is a question which is difficult to answer, and possibly it has not the importance which is often

attached to it. All experience goes to show that the more highly purified a metal is, the more slowly it dissolves in acids, and the theory of " local currents " between the anodic metal and cathodic impurities has received favour in proportion. Pure iron prepared by B. Lambert (*J.C.S.*, 1910, **97,** 2426 ; 1912, **101,** 2056 ; 1915, **107,** 218) was practically uncorroded under conditions where ordinary iron rusted rapidly, but it may be objected that the iron was in the passive state. Very pure aluminium, prepared by J. D. Edwards (*Trans. Amer. Electrochem. Soc.*, 1925, **47,** 287), was practically unattacked by dilute hydrochloric acid. G. D. Bengough, J. Stuart, and A. R. Lee (*Proc. Roy. Soc.*, 1928, **A., 121,** 88) state that spectroscopically pure zinc is resistant to dilute hydrochloric and sulphuric acids, but they attribute the effect of the impurities rather to the lowering of hydrogen overpotential, which is very high at a surface of pure zinc. It may be stated immediately that a simple local current theory, based entirely on the difference of electrode potentials of the two metals forming the couple cannot be maintained quantitatively as an explanation of the difference in the velocity of dissolution.

The fact that commercial forms of zinc dissolve more rapidly than pure zinc in dilute acids was attributed as early as 1830 by A. de la Rive (*Ann. Chim. Phys.*, 1830, **43,** 425) to the effect of local electric currents, and although the theory in its simplest form has failed to offer a quantitative explanation of the facts it has remained largely unassailed in its fundamental features.

T. Ericson-Aurén and W. Palmaer (*Z. physikal. Chem.*, 1902, **39,** 1) modified the theory by taking into consideration the overpotential of hydrogen at the surface of the cathodic metal. When hydrogen evolution occurs through the action of an electrolytic couple the cathodic metal cannot be regarded as

a reversible electrode of that metal, but rather as an irreversible hydrogen electrode. Some metals, whilst having a normal potential sufficiently remote from that of the dissolving metal to form a powerful electrolytic couple, may have so great a hydrogen overpotential that an equipotential state is reached before hydrogen can be evolved in the form of bubbles. Metals having low ·hydrogen overpotentials will facilitate the disengagement of hydrogen, reducing the polarisation of the cell, and if the normal potential of such a metal also differs considerably from that of the dissolving metal the electrolytic couple will be effective. These considerations hold only for that type of corrosion which involves the production of hydrogen gas.

Ericson-Aurén and Palmaer have expressed the rate of dissolution of zinc in dilute acid by the formula

$$V = f\frac{k}{c}\left(\frac{0 \cdot 0576}{n} \log \frac{P_1}{p_1} - \frac{0 \cdot 0576}{n} \log \frac{P_2}{p_2} - \pi_x\right),$$

where V is the velocity, f a constant, k the conductivity of the acid, c the resistance capacity of the cell, P_1 and p_1 the solution pressure and osmotic pressure respectively of the zinc, P_2 and p_2 the solution pressure and osmotic pressure of hydrogen, and π_x is the hydrogen overpotential.

The effect of metallic impurities on the dissolution of zinc in dilute sulphuric acid has been studied by R. Vondráček and J. Izák-Križko (*Rec. trav. chim.*, 1925, **44,** 376), and their results show that copper, iron, antimony, tin, arsenic, and cadmium increase the rate of dissolution, the increase being greatest for copper and least for cadmium. On the other hand, lead and mercury decrease the rate of dissolution, the inhibitive effect of mercury being very strongly marked. It will be

observed that copper and iron, having the lowest hydrogen overpotentials have the greatest accelerating influence, whilst the retarding agents, lead and mercury, have high hydrogen overpotentials. The effect of amalgamating the surface of zinc in reducing its reactivity in reactions involving the formation of hydrogen is well known and finds application in the Leclanché cell.

M. Centnerszwer and M. Straumanis (Z. physikal. Chem., 1925, 118, 415) have investigated the effect of other metals on the velocity of dissolution of zinc in dilute hydrochloric or sulphuric acid by a different method. Instead of adding the metal to the zinc it was added in the form of a salt to the solution of acid, the metal being afterwards precipitated on the surface of the zinc. They found that the metals added could be arranged in the following increasing order of effectiveness in regard to accelerating the reaction : iron < silver < antimony < bismuth < copper < arsenic < cobalt < gold < nickel < platinum. The order is not entirely identical with the order of hydrogen overpotential, but the metals with lowest overpotential (gold and platinum) are found to be the most powerful accelerators. Thallium, cadmium, tin, and lead salts produced no appreciable acceleration. With small concentrations of the salts of the effective metals the acceleration produced was proportional to the concentration, but a limiting value of concentration was soon reached, above which no further acceleration occurred.

M. Straumanis (Z. physikal. Chem., 1927, 129, 370) concludes from measurements of the rate of dissolution of zinc in flowing dilute sulphuric acid in the presence of bismuth, silver, gold, cobalt, and copper, that the effects produced by these metals are not strictly parallel to their hydrogen overpotentials.

The position of the local current theory of metallic dis-
solution was summarised a few years ago by Centnerszwer
and Straumanis (*Z. physikal. Chem.*, 1927, **128**, 369), who
reached the conclusion that the theory of Ericson-Aurén and
Palmaer is in qualitative agreement with the facts, but cannot
be maintained quantitatively. In general, the smaller the
hydrogen overpotential of the cathodic metal, the greater is its
accelerating influence on the dissolution of the metal in acids ;
but the behaviour of a metal cannot be expressed in an exact,
quantitative form. The investigation showed that the poten-
tial of the anodic metal alters during its dissolution and varies
with the current density, which in turn depends partly on the
conductivity of the acid solution. The composition of the
acid solution is also altering during the process. The velocity
of dissolution of the metal in various acids or in the same acid
at different concentrations under otherwise constant conditions
was shown to increase with the equivalent conductivity of
the acid. Experiments in the dissolution of cadmium, iron,
and tin in dilute acid confirmed the results obtained with
zinc.

Another point to be borne in mind is that overvoltages
are generally measured on smooth or slightly roughened sur-
faces and that the values may be very different when the metal
is in a finely-divided state, like that produced by reduction of
a salt or by the selective dissolution of one component of an
alloy. Centnerszwer and Straumanis (*Z. physikal. Chem.*,
1925, **118**, 438) have shown that the hydrogen overvoltage is
considerably lower in the case of a finely-divided metal than
with compact metal, and they relate this to the tendency of
large hydrogen bubbles to collect at a smooth metallic surface,
whilst the gas is freely evolved in the form of minute bubbles

at a matt surface. The finely-divided state of the reduced metal obtained by adding a salt of a nobler metal to the reacting system therefore increases the accelerating effect.

In the author's experience of the formation of contact films of nobler metals on zinc, aluminium, magnesium, etc., either by reduction of a salt solution or by partial dissolution of an alloy it has always been difficult to ensure good contact between the dissolving metal and the sponge of cathodic metal, and this difficulty is intensified by the disengagement of hydrogen, which tends to lift the spongy metal off its support. This effect is observed more with some metals than with others and is particularly noticeable in the case of reduced copper, where not infrequently the greater part of the copper envelope, charged with hydrogen, leaves the surface of the dissolving metal and floats at the surface of the solution. So long as the experimental technique is open to such drawbacks, quantitative agreement can scarcely be expected.

As an illustration of the remarkable acceleration produced by the metals of low hydrogen overpotential, platinum and gold, reference may be made to some experiments described by E. S. Hedges and J. E. Myers (*J. Chem. Soc.*, 1924, **125**, 604). The addition of excessively minute quantities of chloroplatinic acid or chloroauric acid was found to cause a relatively enormous increase in the velocity of dissolution of aluminium in hydrochloric acid. Aluminium foil was first washed in sodium hydroxide solution in order to remove grease, then in water, and afterwards dried and cut into pieces of 8 cm. × 2 cm. These were placed in different reaction vessels containing N-hydrochloric acid and varying minute concentrations of chloroplatinic acid, immersed in a thermostat maintained at 30° C. The metal strips were allowed to dissolve for eighty

minutes and the loss of weight was determined. Some results are given below :—

Concn. of H_2PtCl_6			0	10^{-9}	10^{-7}	10^{-6}
Loss of wt. (mg.)			141·2	174·8	250·3	325·9

It will be observed that a concentration of chloroplatinic acid so small as 10^{-9} causes an increase in the velocity of reaction of more than 20 per cent. Doubtless the platinum is readily reduced to the metallic state at the surface of the dissolving metal and is deposited thereon in an extremely finely-divided state. Some experiments were also carried out on the effect of adding colloidal platinum in small amounts, the final concentrations varying between 10^{-5} and 10^{-12}, and these were found to accelerate the reaction greatly.

Reactions in heterogeneous systems, such as the dissolution of metals in acids, are complex processes, which are controlled by both physical and chemical factors. There is a definite rate of chemical reaction, but if this is rapid the process may be controlled by the rate of diffusion of fresh reactant to the seat of the reaction. Depending on the relative velocities of diffusion and chemical action the process will appear to be controlled either by physical or by chemical agencies. A means of determining which of these is operating is to measure the temperature coefficient of the process. The temperature coefficient of the diffusion process for a rise in temperature of 10° C. is about 1·2, whilst the velocity of a true chemical reaction is practically doubled by a rise of 10° C. When the temperature coefficient is low it is believed that the chemical part of the reaction is rapid and has to wait for fresh material to be supplied by diffusion, and when the coefficient is about 2·0 it is held that the chemical reaction is slower than the rate at which fresh material can be supplied by diffusion.

The temperature coefficient of a complex series of physical and chemical changes is very difficult to interpret, however, and often the values obtained are intermediate between those expected for diffusion or true chemical processes. In the dissolution of metals useful evidence can be obtained by noting the effect of rotating the metal or causing the liquid to circulate. In either case the agitation at the metal-solution boundary ensures an increased rate of replenishment of the acid. If the velocity of the process is controlled by the rate of diffusion of ions or molecules to the metal, it should be increased, therefore, by rotation. On the other hand, the rate of the chemical part of the change will not be affected by the rate of stirring.

Centnerszwer (*Rec. trav. chim.*, 1923, **42,** 579) measured the rate of dissolution of magnesium in dilute hydrochloric acid under different speeds of rotation and found that the velocity of dissolution increases proportionally with the rate of stirring. It is concluded that the velocity of this process is controlled by the rate of diffusion of acid to the metal surface.

The velocity of dissolution of aluminium in hydrochloric acid was studied by M. Centnerszwer and W. Zablocki (*Z. physikal. Chem.*, 1926, **122,** 455), with some remarkable results. The velocity of dissolution was found to depend very little on the rate of stirring and the temperature coefficient was measured as 1·7 to 2·4 for a rise of 10° C. The rate of diffusion of the acid to the metal therefore plays a secondary part, and measurements of the kinetics of the process can be used to interpret the true chemical reaction. The most interesting results obtained are those showing how the reaction velocity varies with the concentration of hydrochloric acid. These results are reproduced in the following table :—

Concentration of HCl (Normality).	Equivalent Conductivity at 18° C.	Percentage of Non-dissociated HCl $(1 - \alpha)$.	Velocity Constant K.	$K/(1 - \alpha)^3$.
0·5	327	14·0	28	0·010
1·0	301	20·8	41	0·005
1·5	—	26·9	290	0·015
2·0	254	33·2	637	0·018
3·0	215	43·4	982	0·012
4·0	181	52·2	1373	0·010

The constancy of the values obtained for the expression $K/(1 - \alpha)^3$ indicates that the velocity of dissolution is proportional to the third power of the concentration of *undissociated* molecules of hydrochloric acid, whilst the table also shows that the velocity is not dependent on the hydrogen-ion concentration or equivalent conductivity of the acid. The reaction is not between aluminium and hydrogen ions, therefore, but between aluminium and undissociated molecules of hydrochloric acid. The data are consistent with the chemical equation

$$Al + 3HCl = AlCl_3 + 3H,$$
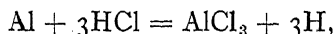
which is followed by the reactions

$$(1)\ 2H = H_2$$
$$(2)\ AlCl_3 \rightleftharpoons Al^{\cdots} + 3Cl'.$$
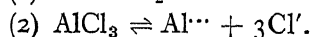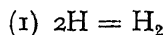
In this scheme ionisation reactions are secondary, and the reaction is determined by the affinity of the anion for the metal. The rather surprising insolubility of aluminium in dilute sulphuric acid is attributed to this cause. The addition of soluble chlorides increases the velocity of dissolution of aluminium in hydrochloric acid probably by repressing the dis-

sociation of the hydrochloric acid and thus increasing the number of *undissociated* molecules.

Measurements were also carried out on the velocity of dissolution of aluminium in solutions of sodium hydroxide, and in this case it was concluded that the reaction is an ionic one represented by the equation

$$Al + OH' + H_2O = AlO_2' + 3H.$$
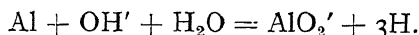
Straumanis (*Z. physikal. Chem.*, 1927, **129**, 370) examined the diffusion effect on the velocity of dissolution of zinc in $N/2$-sulphuric acid by a different experimental arrangement. Instead of rotating the metal in the acid, he kept the metal at rest in a stream of the acid, which was continuously pumped back to the reservoir. In the presence of nickel sulphate and other reducible metallic salts the velocity of dissolution was altered very little by the rate of flow of the acid.

The relative effects of chemical and diffusion processes in the dissolution of metals are well brought out by the experiments of Centnerszwer (*Z. physikal. Chem.*, 1928, **A., 137,** 352) on the velocity of dissolution of cadmium in hydrochloric acid. At the ordinary temperature a concentration of $6N$ is necessary for the evolution of hydrogen to become appreciable. At concentrations not exceeding this value by a great amount the velocity of dissolution is independent of the rate of stirring and the temperature coefficient for a rise of $10°$ C. is about 2. Evidently a true chemical process is being measured. When the concentration of hydrochloric acid is increased to $10 N$ an increase of velocity with speed of stirring becomes apparent, indicating that the diffusion process is now being registered. The same apparent transition from a chemical process to a diffusion process is also brought about by raising

the temperature. The reason for this is that with increasing concentration and rising temperature the velocity of a true chemical process increases much more rapidly than that of diffusion ; hence, whilst at low temperatures and concentrations the chemical reaction may be slow in comparison with the rate of diffusion, at higher temperatures and concentrations the rate of reaction may outstrip the rate of diffusion. It seems reasonable to suppose that this behaviour will be quite general and that in the ordinary way a mixed process will be measured. Similar results were obtained by Centnerszwer (*Z. physikal. Chem.*, 1929, **A.**, **141**, 167) in experiments on the velocity of dissolution of tin in hydrochloric acid.

The dissolution of both cadmium and tin in hydrochloric acid are reactions of the fourth order, and Centnerszwer suggests (*Z. physikal. Chem.*, 1929, **A.**, **141**, 297) that the primary products are anions of the complex acids H_2CdCl_4 and H_2SnCl_4.

Researches on the kinetics of the dissolution of metals tend to concentrate attention on the preliminary diffusion, which enables the reactants to meet, and the chemical reaction itself. But all the conditions for a successful, continuous reaction are not solved thereby. There still remains the disposal of the product of reaction, and provided that a reaction is thermodynamically possible the disposal of the product is the weightiest factor determining its extent and velocity.

In all the systems which have just been discussed the salt produced has been readily soluble in the solution, but these salts are often only slightly soluble in concentrated acids, and then the product adheres to the surface of the metal and hinders the diffusion of fresh acid, so that very slow reaction occurs. The envelope of reaction product may be completely protective, but as a rule it has not the requisite physical properties and

gradually falls from the metal or slowly dissolves in the solution, so enabling the reaction to proceed slowly. The inhibition of the reaction by the product will be discussed in more detail in Chapter V.

The dissolution of metals in acids and other aqueous solutions may be considered theoretically from an entirely different, even if heterodox, point of view. Metals which can liberate hydrogen from acids react very slowly with water at the ordinary temperature, particularly if a salt solution is present and if the metal is finely divided, and in many cases it is possible to establish the production of hydrogen. Very reactive metals, such as the alkali and alkaline-earth metals, react rapidly with water at the ordinary temperature, powdered magnesium does at 100° C., and iron, zinc, and many other metals liberate hydrogen from steam at more elevated temperatures. The less reactive the metal, the more reactive the water has to be made.

Many chemists have at times had suspicions that hydrolytic reactions and other effects usually ascribed to ions might possibly be explained by an increased reactivity of water caused by the added acid, alkali, or salt. Views embodying changes in the complexity and reactivity of water on the addition of electrolytes were developed into a definite theory by H. E. Armstrong, but have not received universal acceptation.

Although the electrolytic dissociation hypothesis and the views of anodic and cathodic processes derived therefrom are on so firm a basis that they show no sign of undergoing revolutionary change, it is well sometimes to consider how far certain phenomena can be consistently explained without its aid. A possible, alternative point of view is that when metals dissolve in dilute acid or other electrolyte solutions with the

evolution of hydrogen the fundamental reaction is between the metal and water, the activity of the water being increased by the presence of the electrolyte. The fundamental reaction may be represented as follows :—

$$Me + xH_2O = Me(OH)_x + xH.$$
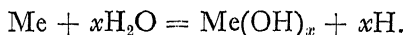
When the product $Me(OH)_x$ is insoluble in the solution, the reaction will stop when the surface of the metal is coated with a thin film, which may be quite invisible, and it will be said that the metal is not soluble in that solution. On the other hand, for dissolution to proceed continuously it is essential that the hydroxide should dissolve in the reagent solution, thus prescribing another function for the electrolyte solution ; it must remove the film of hydroxide as fast as it is formed. Metals giving basic hydroxides will therefore dissolve in acids, those giving acidic hydroxides will dissolve in alkalis, and metals having amphoteric hydroxides may be expected to dissolve in both acid and alkaline solutions. This is, in general, what does occur.

A few examples will make the suggested mechanism clearer. The dissolution of aluminium in hydrochloric acid may be represented by the following series of reactions :—

$$(1) \qquad Al + 3H_2O = Al(OH)_3 + 3H$$
$$(2) \quad Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O$$
$$(3) \qquad\qquad 2H = H_2.$$
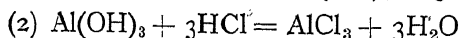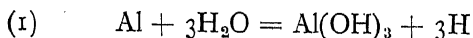
The view is not necessarily inconsistent with the classical theory of electrolytic dissociation, for it matters not whether the hydrochloric acid and aluminium chloride are dissociated or not. The novel feature is the reaction with water to form the hydroxide.

Similarly, when aluminium is placed in sodium hydroxide solution or in sodium carbonate solution it may be supposed that reaction (1) as given above occurs, and that the aluminium hydroxide is removed by the alkali in the form of sodium aluminate as fast as it is produced.   In the case of sodium carbonate, this dissolution will involve the evolution of carbon dioxide, as is observed.

The dissolution of zinc in dilute hydrochloric or sulphuric acid can be pictured in the same way, the primarily formed zinc hydroxide dissolving in the acid.   Zinc hydroxide also dissolves in alkalis, giving sodium zincate, and hence zinc will dissolve in sodium hydroxide.   There is a considerable amount of evidence which goes to show that the sodium zincate solution is a colloidal solution of zinc hydroxide, peptised by sodium hydroxide, and to some extent this colloidal view may be applied to sodium aluminate solutions.   Quite apart from stoicheiometric chemical reactions, therefore, dissolution may be expected to continue if the solution can peptise or loosen the protective film of hydroxide.   This may explain why some metals dissolve more readily in hydrochloric acid than in sulphuric acid.   Chlorides are recognised to be active peptising agents for metallic hydroxides, whereas these are generally precipitated by sulphates.   The purely electrochemical point of view does not explain why aluminium, whilst readily soluble in dilute hydrochloric acid, is extremely slowly attacked by dilute sulphuric acid.   According to the view put forward here, the film of aluminium hydroxide is readily peptised by hydrochloric acid and subsequently dissolves as aluminium chloride.   On the other hand, the film of hydroxide is not peptised, but rather is coagulated by sulphuric acid and hence its disintegration is very slow, so that it dissolves at a slow rate

in the sulphuric acid.   It may be stated that colloidal aluminium hydroxide in the form of a gel is rapidly brought into solution by the addition of a little hydrochloric acid, whilst a colloidal solution of aluminium hydroxide is precipitated by sulphuric acid.   K. Jablczynski and E. Hermanovicz (*Rocz. Chem.*, 1926, **6**, 466) have shown that the velocity of dissolution of aluminium in 0.1 *N*-sodium hydroxide is 18.5 times as great as that in hydrochloric acid of the same concentration.   This result is difficult to interpret electrochemically, but the superior peptising action of alkalis is well known.

Iron dissolves in dilute hydrochloric and sulphuric acids, in which the hydroxide is soluble.   The hydroxides of iron are not soluble in dilute solutions of sodium hydroxide and the metal is unattacked by alkaline solutions.   In fact, solutions of alkalis render iron definitely *passive*, which, as will be shown later, is due to the formation of a highly protective film of ferric oxide or hydroxide.   The action of nitric acid on iron will be discussed fully in Chapter V.

The behaviour of magnesium is particularly interesting. The hydroxide is soluble in dilute acids and as would be expected the metal readily reacts with dilute acids, evolving hydrogen.   The hydroxide is insoluble in alkali solutions and the metal does not react.   Magnesium hydroxide is soluble, however, in a number of salt solutions, including sodium chloride and especially solutions of ammonium salts.   Magnesium metal is found to dissolve at the ordinary temperature in solutions of these salts with the evolution of hydrogen. Magnesium dissolves very readily in solutions of ammonium chloride, a solution which readily dissolves magnesium hydroxide.

The alkali metals, the only metals having freely soluble

hydroxides, react readily with water in the absence of added electrolytes ; with metals like calcium and other alkaline earths, where the hydroxide, although very soluble for a metal hydroxide, soon reaches saturation in solution, the reaction, rapid at first, soon becomes relatively slow. If, however, sufficient acid is added to dissolve the hydroxide, the dissolution of the metal proceeds rapidly and continuously.   The oxides and hydroxides of the alkali metals are also soluble in the simple alcohols, giving rise to methoxides, ethoxides, etc., and the alkali metals react with these alcohols with the evolution of hydrogen.

It appears, therefore, that there is a parallelism between the hydrogen evolution type of dissolution of metals and the solubility of the oxide of the metal in the corrosive solution. Apart from this parallelism, the theory which has been put forward has no experimental foundation, but it does fit the facts and has on several occasions proved of practical service in predicting the behaviour of metals exposed to aqueous solutions.   The theory of preliminary reaction with water is to be regarded merely as a suggestion and the true explanation may prove to be quite different.

The Periodic Dissolution of Metals.

At the beginning of the present century, W. Ostwald (*Z. physikal. Chem.*, 1900, **35**, 33, 204) described the periodic dissolution of chromium in dilute acids.   The alternate periods of rapid and slow evolution of hydrogen were obtained only with one particular batch of chromium and the phenomenon was traced to the presence of some unknown impurity in the metal.

E. S. Hedges and J. E. Myers (*J. Chem. Soc.*, 1924, **125,**

604 ; 1925, **127,** 445) recorded automatically and continuously the rate at which hydrogen is evolved in numerous reactions of this type and found that under certain conditions periodicity is a general feature of these reactions and that chromium does not form a special case.*

The following reactions were found to be periodic under certain conditions : the dissolution of zinc, iron, aluminium, manganese, and cadmium in hydrochloric acid ; zinc and magnesium in sulphuric acid ; aluminium and magnesium in orthophosphoric acid ; calcium, sodium amalgam, and aluminium amalgam in water ; magnesium and zinc in ammonium chloride solution ; aluminium in cupric chloride solution ; magnesium in dilute nitric acid ; magnesium in acetic acid ; sodium in ethyl alcohol ; sodium in n-butyl alcohol ; aluminium in solutions of sodium hydroxide, barium hydroxide, and potassium carbonate ; copper, nickel, cobalt, and iron in mixtures of hydrochloric and nitric acids of certain compositions. This list of reactions includes not only several different metals, but also comprises acid, alkaline, and neutral aqueous solutions and alcohols.

The pronounced periodicity in the rate of evolution of hydrogen is illustrated by Fig. 4, which shows automatic records of the pressure at which hydrogen is evolved in several of the reactions. In each case the portion of the record shown represents a time interval of 8·5 minutes.

In order to obtain a more complete representation of the reaction curve, some measurements of the rate of hydrogen evolution were made by taking readings of the pressure on an aniline manometer every 15 seconds. One of the graphs

* A full account of these investigations is given in Hedges and Myers' " The Problem of Physico-Chemical Periodicity," 1926, Arnold & Co.

constructed from these data, representing the dissolution of aluminium in N-hydrochloric acid, is reproduced in Fig. 5. The decrease in the frequency of the periods during the course of the reaction is readily apparent in the graphs constructed in this way. The frequency was also found to decrease with decreasing concentration of the reagent, with lowering of temperature, and with the addition of very small amounts of catalyst poisons, such as potassium cyanide and arsenious acid.
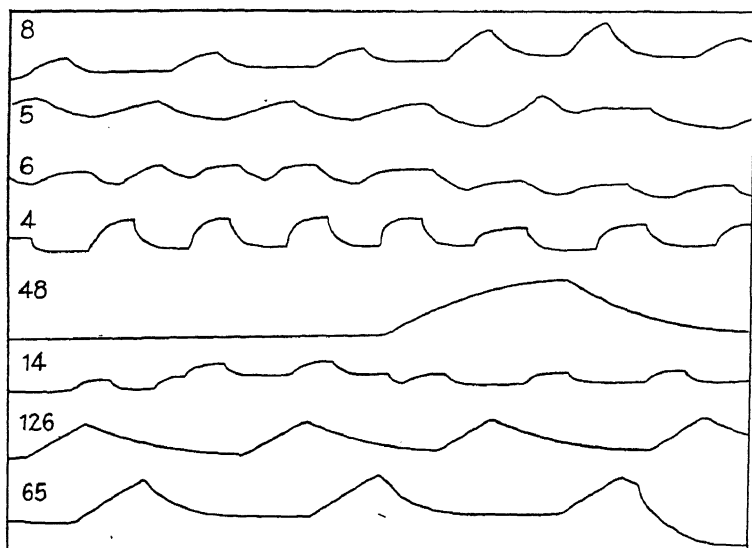
FIG. 4.—Automatic records of the periodic dissolution of metals.

The cause of these periodic phenomena has never been completely elucidated, and subsequent research was directed to the study of the anodic dissolution of metals under the external application of a current, where the velocity of dissolution and other factors can be kept under control. The anodic periodic phenomena will be discussed in Chapter VI., where it will be shown that the periodicity is in all cases connected with the alternate formation and disappearance of a

protective film (not necessarily of oxide) over the surface of the metal. If the ordinary dissolution of metals in the absence of externally applied current is in reality an anodic process, it may be that the periods observed are to be explained by the alternate formation and dissolution of a film. The phenomena might readily be explained on such grounds if the metal reacts
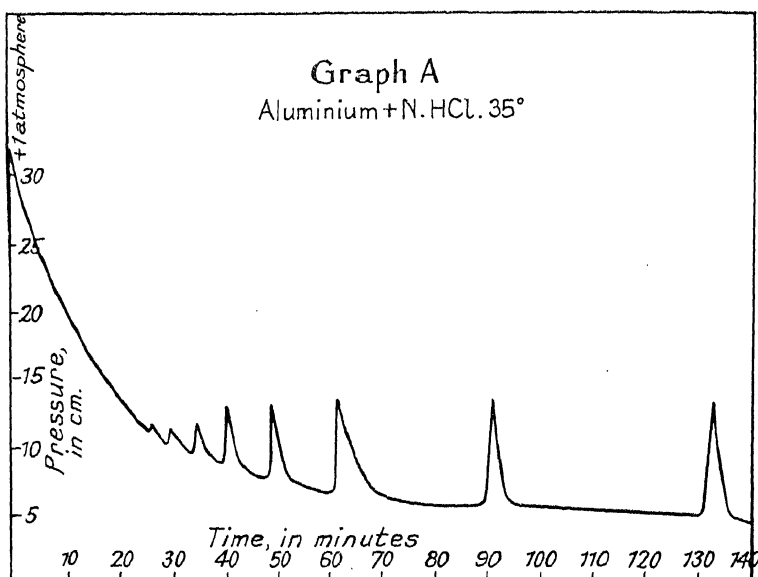
FIG. 5.—The periodic dissolution of aluminium.

with water in a way similar to that suggested in the preceding section.

Although the special conditions required for this type of periodicity were not completely elucidated, the experiments rendered it quite clear that the periods are obtained only in the presence of some foreign substance, which may be present in extremely small amount. In some cases it was evident that the glass reaction vessel was capable of furnishing the requisite trace of " catalyst," whilst in others the addition of

colloids in so small an amount as one part in a million brought about periodicity. Colloids are known to be strongly adsorbed at the surface of metals, and the adsorbed matter might conceivably form a film which was broken down periodically by the acid. Alternatively, the adsorbed colloid might stabilise temporarily an oxide or hydroxide film at the metal surface. Another condition which brought about periodic dissolution was contact of the dissolving metal with a more noble metal, which had previously been " activated " by heating in a vacuum, by cold-rolling, by bombardment of the surface with cathode rays, or by coating with metal by electrodeposition at high current densities. The behaviour of these metallic couples is closely in line with the purely anodic dissolution of metals described in Chapter VI., and may conceivably likewise be connected with the formation of oxide films.

Corrosion in Salt Solutions.

As a rule the presence of oxygen is necessary for the continuance of corrosion of metals in neutral or nearly neutral salt solutions. Natural waters are usually saturated with air and the requisite condition is provided. The corrosion product consists mainly of hydroxide with varying amounts of basic salts, but the product is not the result of direct oxidation of the metal, but is formed by a secondary process. Direct oxidation gives a uniform coating of oxide, which protects the underlying metal from further attack, but the rust produced by the secondary process described below is localised at certain spots and is actually produced not in real contact with the metal surface but in the solution in its vicinity ; hence the corrosion product has no protective value.

The mechanism can best be described by imagining the

corrosion of a bar of iron, containing fragments of copper, immersed in a solution of sodium chloride, which contains dissolved oxygen. This artificial system is analogous to the exposure of iron-work to sea-water or salt-spray and has therefore some practical importance. The copper or other relatively noble metallic inclusions act as cathodes and the adjacent areas of iron act as anodes. At the anodic areas chlorine ions are discharged and react with the iron to form ferrous chloride. At the cathodic areas sodium hydroxide and hydrogen are formed, the hydrogen being removed by oxidation through the dissolved oxygen at a rate which largely determines the rate of corrosion. Thus, at adjacent areas on the bar there are produced solutions of ferrous chloride and sodium hydroxide, respectively. Where these solutions meet ferrous hydroxide will be precipitated in the form of a membranous film, which will not be in good contact with the metal, because it is not formed directly at the metal surface, but some way out in solution, where the ferrous and alkaline solutions meet. Ferrous hydroxide does not remain long as such, but rapidly oxidises to ferric hydroxide under the influence of the dissolved oxygen.

These considerations are applicable to the corrosion of other metals under similar conditions. It is to be expected that rust produced in this way will not protect the remaining metal from further attack, and as the salt is regenerated simultaneously with the precipitation of the hydroxide it is probable that corrosion will proceed very deeply. Indeed, the presence of rust in certain places may tend to hasten corrosion by causing a lack of homogeneity in the supply of oxygen over the surface of the specimen, an effect which will be discussed more fully below.

In this discussion the presence of noble heterophase im-

purities has been assumed, and in ordinary commercial metals this assumption is generally justified, but this is not the only condition leading to the establishment of an electro-motive force when the specimen is immersed in an electrolyte solution. Differences of potential can be set up even in chemically homogeneous metals by physical heterogeneities. These may always be expected except in single crystals. The potential of a metal varies slightly with its physical state and may be altered quite appreciably by cold-working, for instance. Usually, the cold-worked metal is somewhat more negative than the annealed metal. An unequally annealed metallic article, or one which has undergone deformation or strain in localised spots, will therefore behave to some extent as an article composed of two different metals. Strained areas will become anodic and annealed areas cathodic.

Differences in concentration of a solution may also cause corrosion currents to be set up in the way described on page 15.

There is yet another factor which is involved in the production of potential differences in systems to which oxygen has access and which can operate even when the metal is both chemically and physically homogeneous. This is embodied in the " differential aeration principle " of Evans, a principle which will be discussed in some detail, as it has a very wide applicability to problems of corrosion and is directly concerned with the production of protective films on metals.

The Differential Aeration Principle.

The principle may best be described by reporting an experiment to which U. R. Evans (*J. Inst. Met.*, 1923, **30**, 261) refers as his " key experiment." Two strips of iron, cut from the same sheet, were rubbed with emery paper, wiped with filter

paper and immersed in the two compartments of a cell divided by a porous partition. Both compartments were filled with $N/2$-potassium chloride and the two strips were connected to the terminals of a milliammeter. When bubbles of air (free from carbon dioxide) were passed over one of the iron strips a current of electricity was set up and registered on the milliammeter, the aerated strip becoming the cathode and the unaerated strip the anode. The unaerated electrode also dissolves during the experiment, as can be shown by weighing it before and after. A similar result can be obtained with other metals.

The important fact which this experiment establishes is that the presence of oxygen alters the potential of a metal, rendering it electropositive to a specimen of the same metal immersed in the same solution in the absence of oxygen. Thus, a *differential aeration current* may be set up between two otherwise similar electrodes, or between two portions of the same metal to which oxygen is supplied at different rates. Another important point established is the direction of the current, which is provided by the consumption of metal from the *unaerated* electrode. That is to say, the portions to which oxygen has least ready access are those where corrosion is greatest. This conclusion may at first sight seem almost paradoxical, but the action of oxygen is of the direct chemical type, giving at the aerated portions a uniform film having some protective qualities. These parts are thus ennobled and the parts sheltered from oxygen are relatively electronegative and dissolve by anodic attack of the ions in solution.

The differential aeration principle supplies a ready explanation of many facts in corrosion which are difficult to understand in any other way. In the ordinary way even a chemically

pure metal free from strain has not a perfectly continuous surface, but contains scratches and crevices due to grinding or other causes. Even when subsequently polished, these crevices are not completely eliminated, but are often imperfectly bridged over by a film of worked metal, leaving perhaps minute perforations. Cavities formed in the metal in this way are particularly inaccessible to oxygen and therefore become anodic to the surrounding metal, to which atmospheric oxygen can diffuse. The corrosion then becomes concentrated at such spots, with the result that the cavity becomes deeper and deeper and the phenomenon of " pitting " occurs. The porosity of the surface of a metal is, therefore, an important factor in its tendency to corrosion. Minute cracks and imperfections existing at the junction of two dissimilar metals also provide areas of metal relatively inaccessible to oxygen, and corrosion will tend to concentrate on such metal joints quite independently of the difference of potential set up by the contact of the two metals. This explains why at a metal joint sometimes both metals are found to be corroded. Many examples of the application of the differential aeration principle to some of the most important problems of corrosion are given by Evans in his book " Corrosion of Metals " (Arnold, 1926), which should be consulted for further details. Evans emphasises that the continued supply of oxygen to the cathodic portion is needed for the maintenance of the current, that is, for the continuance of corrosion at the anodic portion. The current strength is determined mainly by the rate of supply of oxygen, and if the cathodic area is large and the layer of liquid shallow, the current produced may be considerable. If the number of inaccessible parts is small, the current will be concentrated at these spots and very severe pitting may

result; if there are numerous crevices to which oxygen has little access, the degree of penetration in a given time will be correspondingly smaller.

The material discussed in this Chapter shows not only that there are several ways in which corrosion can occur, but also that the careless application of protective films may make matters worse by concentrating corrosion at certain spots, where the attacks may penetrate very deeply.

In a recent study of the corrosion of zinc in solutions of potassium chloride in the presence of oxygen, G. D. Bengough, A. R. Lee, and F. Wormwell (*Proc. Roy. Soc.*, 1931, **A., 131,** 494) describe results which, it is maintained, cannot be adequately accounted for by differences in oxygen concentration as postulated by the differential aeration theory, and a modified view of the mechanism is proposed.

It is considered that the initial behaviour of zinc, when placed in a salt solution which does not form a passivating film, either local or general, is to displace hydrogen at a multiplicity of points. Neglecting the possibility of the production of gaseous hydrogen, a polarising layer is formed at the metal surface. The oxygen is required for depolarisation and the anions must be such as to form a soluble salt of the metal ; corrosion will then proceed at a rate directly proportional to the oxygen supply, provided that the concentration of anions is sufficient and no protective films are formed.

The film of zinc hydroxide formed in the corrosion of zinc in solutions of potassium sulphate or chloride in the presence of oxygen is in parts continuous, impermeable to oxygen and closely adherent to the metal, and in parts in the form of " domes," which are loose and permeable to oxygen. Corrosion is most serious under the " domes." The authors point out

that, if the protective type of hydroxide film is formed over a part of the metal, corrosion can only occur elsewhere, and maintain that the preferential corrosion at the portions of the metal covered by the " domes " is not due mainly to a potential difference set up by difference of oxygen concentration, but to the fact that ions can freely enter solution there.   Other portions are covered with a precipitated protective film which prevents local solution of the metal, but allows depolarisation of hydrogen displaced by metal entering the solution elsewhere. Actually, more oxygen reaches the metal beneath the loosely adherent domes than that beneath the protective film.

Simultaneously, there appears a paper by U. R. Evans, L. C. Bannister, and S. C. Britton (*ibid.*, 1931, **A., 131,** 355) in which it is shown experimentally that, under conditions favourable for the complete tapping of the electric currents flowing between the anodic and cathodic portions of corroding metal, the currents measured are equivalent to the corrosion produced, both in cases where the anodic and cathodic areas consist of different metals, and when the anodic and cathodic areas of the same metal are determined by differences in oxygen concentration.   The problem of corrosion velocity thus resolves itself into a study of the electrochemical factors which determine the strength of this current.

The results of further researches along both of these lines will be awaited with great interest.

CHAPTER III.

THE PROTECTIVE EFFECT OF OXYGEN ON METALS.

A CONSIDERABLE variety of behaviour is manifested in the reaction of different metals towards oxygen, for some, such as platinum and gold, are apparently unchanged by oxygen even at high temperatures, whilst others, such as the alkali metals, burn vigorously in oxygen at relatively low temperatures. One determining factor, important in all heterogeneous chemical reactions, is the degree of subdivision ; for some metals, which in the compact state are only superficially oxidised when heated in air or oxygen, can be obtained as a fine, pyrophoric powder, which burns spontaneously when brought into the air. This is due not only to the fact that a great amount of such a metal is at the surface, so that superficial oxidation must consume most of it, but also that the enormous surface exposed involves a considerable heat of adsorption of oxygen.

Apart from the physical state of the metal, at least three factors will determine the result : (*a*) the chemical affinity of the metal for oxygen, (*b*) the volatility of the metal, and (*c*) the physical properties of the oxide. The alkali and alkaline-earth metals combine a strong chemical affinity for oxygen with a relatively high volatility, and consequently burn readily when heated in the air. Mercury, although highly volatile for a metal, does not possess the requisite affinity for oxygen. Aluminium is an example of a metal which has

a high chemical affinity, but the physical properties of the oxide product formed at the surface prevent further rapid oxidation of the massive metal.

This third factor is the most difficult to assess, since the physical properties of the oxide may vary with the conditions of production, but in general, if a hard, compact skin of oxide forms it may protect the underlying metal from further oxidation by preventing the diffusion of more oxygen. One of the properties involved is specific volume, a fact rendered clear by the work of N. B. Pilling and R. E. Bedworth (*J. Inst. Metals*, 1923, **29**, 529), who were able to correlate the protective effect of an oxide film with the relative densities of the metal and the oxide. If the formation of the oxide is accompanied by a decrease of volume, the oxide film must shrink and crack, so providing channels for the further access of oxygen. Such a film will not be protective. When, however, the formation of the oxide involves an expansion, the underlying metal will at all times be covered by the film of oxide, which can exert a protective effect. At the same time, if the increase of volume is large, the expansion involved may easily cause cracking of the film and the coating will be poorly protective. From a consideration of the densities of the metals and their oxides, non-protective oxide films are to be expected in the cases of lithium, sodium, potassium, magnesium, calcium, strontium, and barium, all of which, as is well known, can be burned completely in oxygen without difficulty.

In addition to the specific volume, another property which determines the protective effect of an oxide film is probably a specific adherence of the oxide to the metal. It is to be expected that the adherence will depend in part on the relation of the space lattice of the oxide to that of the metal, being

greatest, perhaps, where these are similar. Protective oxide films are as a rule so thin that it is difficult to gain any information about their crystal structure, and, as will be seen later there is reason for the belief that in some cases at least the film is amorphous. Some such considerations must explain why aluminium, although normally exceedingly resistant to atmospheric oxidation by reason of the protective properties of the oxide film which forms over its surface, when in the presence of mercury sprouts alumina at such a rate that the reaction has been adapted to make an amusing toy. The same oxide is present, but it has a different relation to the underlying metal.

Pilling and Bedworth (*loc. cit.*) showed theoretically that where a protective oxide film is formed the rate of growth of the film should be inversely proportional to the thickness of the film at a given moment, since the rate of growth of the film is regulated by the rate of diffusion of oxygen through it. This leads to a parabolic curve relating thickness of film to time. The increase of weight upon heating copper in oxygen was measured at different time intervals and was found to be parabolic at temperatures above 700° C. At lower temperatures irregularities occurred, which were attributed to the cracking of the film. At higher temperatures the film is probably plastic and does not crack. The protective film consists mainly of cuprous oxide, with a certain amount of cupric oxide on the outside. Metals which produce nonprotective oxide films, such as calcium and magnesium, were found to increase in weight steadily on oxidation, the curves connecting increase of weight with time being straight lines. Aluminium exhibited a peculiar behaviour when heated at 600° C., forming an oxide film for a time, after which further

oxidation suddenly ceased, the thickness of the oxide film then being 0·00002 cm. It has been suggested that this behaviour is probably due to a change in the physical character of the oxide, which renders it impermeable to oxygen. In a further paper, Pilling and Bedworth (*Ind. Eng. Chem.*, 1925, **17,** 372) show that the oxidation of both nickel and copper by oxygen at about 1000° C. is in accordance with the parabolic law, copper oxidising about thirty times as fast as nickel. The rate of oxidation was measured by determining the increase in the electrical resistance of a standard wire test piece as well as by the increase of weight.

J. S. Dunn (*Proc. Roy. Soc.*, 1926, **A., 111,** 203, 210) found that the rate of oxidation of alloys of copper and zinc between 600° and 900° C. is given by $Ae^{-Q/RT}$, where T is the absolute temperature and A and Q are constants. This expression can also be deduced theoretically, assuming the mechanism of the oxidation to be the diffusion of oxygen through a protective film of cuprous oxide. This diffusion does not appear to occur through the intermediate formation of cupric oxide. Dunn also found that the parabolic equation holds for the low temperature oxidation of copper between 200° and 300° C., but that catalytically active copper oxidises more rapidly than ordinary copper and does not follow the diffusion law unless it is annealed above 400° C. There are other cases where it has been reported that the rate of growth of the oxide film does not appear to be controlled entirely by the rate of diffusion of oxygen through the film, such as the work of W. G. Palmer (*Proc. Roy. Soc.*, 1923, **A., 103,** 444) on the oxidation of copper. Evans (" Corrosion of Metals," 1926, p. 14) has suggested a general equation connecting the film-thickness y with the time t in the form

$$\frac{dy}{dt} = \frac{c_0 k_0 k_1}{k_0 + y k_1},$$

where k_0 is a physical constant and k_1 a chemical constant. This reduces to the parabolic form when k_0 is small compared with $y k_1$, and to a linear form when $y k_1$ is small in comparison with k_0, but also provides for curves which are neither simply linear nor parabolic. W. H. J. Vernon (*J.C.S.*, 1926, 2273) has obtained results for the low temperature oxidation of copper which conform well with Pilling and Bedworth's equation for the relation between temperature and rate of oxidation, viz.

$$K = A T^n,$$

where K is the rate constant (square of weight increment per unit area per unit time), T the absolute temperature, and A and n are constants, but the results are in perfect agreement with Dunn's equation

$$d \log W / dT = - Q / R T^2,$$

where W is a linear function of weight increment, T the absolute temperature, and Q and R are constants.

W. Feitknecht (*Z. Elektrochem.*, 1929, 35, 142) has made an X-ray and microscopical examination of the layer produced by the oxidation of copper at elevated temperatures, and concludes that the film consists of cuprous oxide, having a crystal structure similar to that of the metal, which subsequently becomes covered with a thin layer of cupric oxide. Over the temperature range 850°-1020° C. the relation $x^2 = Kt$ (where x is the amount of oxygen taken up by the copper in the time t, and K is a constant) was found to hold only after the lapse of some time. The variation of the velocity constant with temperature could not be represented satisfactorily by Dunn's equation. Experiments in which mixtures of oxygen

with nitrogen and with carbon dioxide were used showed that, provided the partial pressure of the oxygen was greater than the dissociation pressure of copper oxide at the particular temperature, the velocity coefficient was independent of the oxygen pressure, but became approximately proportional to the logarithm of the partial pressure when it fell below the dissociation pressure.

Films are thickened by any condition which tends to keep the oxide film pervious to oxygen.   C. N. Hinshelwood (*Proc. Roy. Soc.*, 1922, **A., 102,** 318) showed that on alternate exposure of copper to oxygen and hydrogen at 233° C., oxygen was taken up more rapidly at each successive stage.   W. G. Palmer (*ibid.*, 1923, **A., 103,** 444) found that mixtures of oxygen and hydrogen oxidise copper more readily than oxygen alone. U. R. Evans (*J.C.S.*, 1925, **127,** 2484) has described the production of visible oxide films on copper at the ordinary temperature by the combined action of oxygen and cathodic treatment.

The Protective Oxide Film on Copper.

As early as 1923, W. H. J. Vernon reported the existence of an invisible, protective oxide film formed by heating copper for one hour at 100° C. (compare Vernon, *British Non-Ferrous Metals Research Association*, Research Report No. 4, 1927, p. 6), but the results of the further investigation of this film were not published until 1926 (*J.C.S.*, 1926, 2273).   Since this research forms the starting-point of a good deal of subsequent investigations it will be described in some detail.

Sheets of high-grade electrolytic copper measuring 10 cm. $\times$ 5 cm. $\times$ 1·25 mm. were freely suspended in an electric muffle furnace and heated for approximately one hour at the

desired temperature, which varied between 50° and 250° C. After heat-treatment the specimens were freely suspended in a tarnishing atmosphere, typical of winter-time town air, containing traces of sulphur compounds, but free from excessive local pollution. The temperature was well above the dew-point throughout the duration of the exposure. The visible results after twenty days' exposure to the tarnishing atmosphere are shown in the following table :—

(1) Unheated copper   . Tarnished a reddish-purple colour.
(2) Heated at 55° C.   . Same result as (1).
(3) Heated at 75° C.   . No change: *practically unaltered copper.*
(4) Heated at 100° C.   . No change since heat-treatment.
(5) Heated at 125°-250° C. No change since heat-treatment.

The table shows the striking result that heating copper in air at a temperature as low as 75° C., whilst having practically no visible effect on the metal, serves to inhibit tarnishing on subsequent exposure to the atmosphere. Taken in conjunction with the measured increase of weight during the heat-treatment, it is justifiable to conclude that the protection is afforded by a film of oxide so thin as to be normally invisible. Vernon has attempted an estimate of the thickness of this film from the available data at 55° C. :—

Weight of oxygen absorbed $= 0.007$ mg. per sq. dm.
Weight of equivalent Cu_2O $= 0.063$ mg. per sq. dm.
Volume of equivalent Cu_2O $= 1.05 \times 10^{-5}$ c.c. per sq. dm.
Hence, thickness of Cu_2O film $= 1.05 \times 10^{-7}$ cm. $= 10.5$ Å.

This result is of the same order of magnitude as the lattice dimension of cuprous oxide, 4·26 Å. It must also be pointed out that the actual emeried surface is greater than that measured, being very possibly double. Vernon suggests, therefore, that *the minimum thickness of film necessary for protection may be such that the unit lattice of the oxide is completed for the whole surface.*

The following table, showing the weight-increments of specimens exposed to a tarnishing atmosphere subsequently to heat-treatment, illustrate in a striking way the protection afforded by the film formed at 75° C. and above :—

PERIOD OF EXPOSURE AND INCREASE OF WEIGHT
(MG. PER SQ. DM.).

Temperature of Heating.	6 Days.	34 Days.	100 Days.
—	0·29	0·91	1·28
50° C.	0·21	0·76	1·12
75	0·00	0·30	0·42
100	0·00	0·17	0·31
125	0·00	0·11	0·28
150	0·00	0·15	0·24
200	0·00	0·12	0·22
250	0·00	0·19	0·26

Cleaned specimens of copper exposed for one month to a relatively pure atmosphere were found to be resistant to tarnishing in a polluted atmosphere. The protective oxide film therefore forms slowly on copper at the ordinary temperature.

Similar experiments were conducted with specimens of *brass* heated between 200° and 425° C., and definite evidence was obtained that the protection extends to brass, although the oxide film in this case is not so efficacious as that on copper, the effects being confined mainly to the suppression of further colour changes.

The effect of an invisible oxide film on the chemical behaviour of copper was demonstrated by Evans (*J.C.S.*, 1925, **127**, 2491) in a different way. Copper exposed to dry air

for 17 hours was found to be darkened by $N/25$-silver nitrate much less quickly than was freshly ground copper, an effect which was attributed to oxidation, since exposure to carbon dioxide had no such effect.

F. H. Constable (*Nature*, 1929, **123**, 569) describes an experiment which confirms the work of Vernon. When a mixture of 1 volume of hydrogen sulphide and 5 volumes of air is passed over reduced copper, two complete colour sequences are produced in a few minutes ; but if the copper surface is left exposed to the air for some hours previously, the hydrogen sulphide mixture produces little effect.

The Protective Oxide Film on Aluminium.

The existence of an oxide film of highly protective value at the surface of aluminium which has been exposed to the air or oxygen has long been suspected. Aluminium is normally a very reactive metal and is difficult to reduce from its compounds. The resistance of this metal to oxidation at high temperatures and its resistance to many types of atmospheric corrosion could be understood only by supposing the surface to be covered by a thin, invisible oxide film, forming a continuous and adherent coating. This view was supported by the poor electrical contact between pieces of aluminium and by the observation of an induction period in the dissolution of aluminium in acids. From observations on the preliminary slow dissolution of aluminium in hydrochloric acid, Centnerszwer (*Z. physikal. Chem.*, 1926, **122**, 455) concluded that the thickness of the passive layer is not of molecular dimensions, but is about 0·003 cm. This result was obtained by measuring the amount of aluminium dissolved during the induction period and can scarcely be expected to furnish a

value for the thickness of the oxide film, but merely gives the amount of aluminium dissolved before the protective oxide film is completely destroyed. One is inclined to expect that on immersion in acid the film will become more and more porous, the underlying metal meanwhile dissolving in greater proportion, until the film is entirely or almost entirely dissolved, marking the end of the induction period. Whilst the thickness of the layer dissolved during the induction period is of much interest, it is clearly not safe to suppose that it represents the thickness of the protective film.

R. Seligman and P. Williams (*J. Inst. Metals*, 1920, **23,** 169) have shown that the presence of a film of oxide on aluminium which has been heated in a muffle at 800° C. may readily be demonstrated. Foil so treated is indistinguishable from unheated foil when viewed by reflected light, but when examined by transmitted light the foil appears transparent, with a number of beads of unchanged metal held in place between the layers of oxide. On heating the foil with concentrated nitric acid the remaining metal may be dissolved out and the oxide left as a mass of colourless, iridescent scales.

The oxide film produced by the anodic oxidation of aluminium (see p. 183) has been isolated by H. Sutton and J. W. W. Willstrop (*J. Inst. Metals*, 1927, **38,** 259 ; *Nature*, 1927, **119,** 673), using a simple and very neat method, which consisted in volatilising the metal as chloride and leaving an envelope of the thin, continuous surface film. A piece of the anodically treated aluminium sheet was cut into narrow strips that were put into a silica boat, which was introduced into a hard-glass tube mounted in a furnace. Pure, dry hydrogen was passed through the tube until all the air had been expelled and then the temperature of the tube was raised to 300°-320° C. and

maintained at that value while a slow stream of dry hydrogen chloride was passed through, the hydrogen then being stopped. The aluminium at the exposed edges of the strips was readily attacked by the hydrogen chloride, with the formation of hydrogen and aluminium chloride, the latter being removed as a vapour at the temperature of the experiment.

In order to determine the weight of film formed by any particular treatment it was necessary to perform a blank experiment with untreated aluminium, which was found to give a small residue, due to atmospheric oxidation of the aluminium surface and to impurities in the metal. Iron and silicon in the aluminium are volatilised with the aluminium in the form of their chlorides.

The films isolated had a greyish colour, due to traces of carbon, becoming pure white after ignition in the air. The thickness of the films examined varied from 0·0000033 to 0·0002 cm., the film produced by the standard anodic treatment being about 0·0001 cm. thick. The film was shown to consist of oxide and not of hydroxide.

W. H. Withey and H. E. Millar (*Nature*, 1927, **119**, 123) had previously used a practically identical method for determining the proportion of oxide in aluminium and showed that most of the oxide was located at the surface, being left in the form of a white shell. L. C. Bannister (*J.C.S.*, 1928, 3163) made unsuccessful attempts to isolate oxide films on tungsten and molybdenum by a similar method.

U. R. Evans (*J.C.S.*, 1927, 1039), using the methods described in detail later in the present chapter, has isolated the oxide film normally present on aluminium which has been exposed to the air. The films isolated were in the form of transparent flakes, containing much opaque residual metal, the structure bearing signs of the original grinding.

Vernon's work on the formation of a protective film on aluminium during exposure to the air is described on page 86.

The Colours of Thin Films of Oxides.

When metals are heated in the air gently, so that only a thin film of oxide is produced, in many cases a series of colours is produced on the surface of the metal. These " temper colours " have long been familiar to steel-workers and have been used as an indication of the temperature attained, although they depend on the duration of heating as well as on the temperature. The colours have for many years been supposed to be due to interference of light by the reflection of light at both the outer and inner surfaces of the thin oxide film. When the film has a thickness of the order of magnitude of a wave-length of light the rays reflected from the two surfaces of the film may be out of phase and a certain colour may therefore be extinguished, leaving a balance of coloured light. The problem is discussed fully in text-books of physics. The interference view of the production of temper colours has been questioned at times (compare Mallock, *Proc. Roy. Soc.*, 1918, **A., 94,** 566), but general agreement has now been reached that this is the true explanation. (Compare D. H. Bangham and J. Stafford, *Nature*, 1925, **115,** 83 ; F. H. Constable, *Proc. Roy. Soc.*, 1927, **A., 115,** 570 ; U. R. Evans, *Nature*, 1927, **120,** 584.)

Particularly convincing evidence has been obtained by Evans (*Proc. Roy. Soc.*, 1925, **A., 107,** 228), who showed that the temper colours on steel can be changed in the correct inverse sequence by cathodic treatment in dilute hydrochloric acid. Similar colours can be obtained on molten lead, even under conditions when the oxide film is molten, an observation

which disposes of Sir C. V. Raman's view that the colours are due to a granular structure (*Nature*, 1922, **109,** 105). Evans showed that the oxide film can be removed bodily from the surface of molten lead, and that the colours then seen by transmitted light are complementary to those viewed in reflected light.

The interference tints on copper commence in the sequence : brown, reddish-mauve, blue, greenish-silver ; then follow the second order colours, yellow, rose, blue, green ; there is usually a further alternation between rose and green, and then the colour becomes a dull pinkish-grey, which is probably the characteristic colour of the oxide. These films were isolated by Evans (*Nature*, 1929, **123,** 16) by removing the enclosed metal through anodic treatment in potassium sulphate solution, and were found to consist of cuprous oxide, which is transparent within the interference-colour range. Opaque areas, due to metallic copper, were observed in films showing the first-order tints. Cupric oxide, which is formed under strongly oxidising conditions, obscures the colours.

Interference colours are not confined to thin films of oxides, but have been observed also in the films formed by the action of iodine vapour and hydrogen sulphide on metals.

The Protective Oxide Film on Iron.

The immunity afforded by the presence of an oxide film is not confined to oxygen, but extends to attack by other chemical agents. For example, when drops of dilute copper nitrate solution are placed on iron, which has been heated very gently in the air so as to give it a thin coating of oxide, metallic copper is not deposited immediately, although the deposit on a pure iron surface is immediate. This method of testing has been

applied by Evans (*J.C.S.*, 1927, 1021) to the examination of the protective properties of the oxide film on iron, and the greater part of our knowledge of this film is due to his work.

When a strip of pure iron is heated in the air at one end only, a visible scale of oxide forms at the heated end, gradually becoming thinner as it progresses towards the cold end, where the metal appears to be unchanged, and in the intermediate region are to be observed temper colours, due to the interference of light by a thin film of oxide.

When the different parts of the cooled strip are tested with drops of copper nitrate solution it is found that metallic copper is immediately deposited at the end which has not been heated, but that further along the strip, and before the temper colours are reached, the deposit becomes less and less and eventually ceases, although this part is not visibly different from the part where copious deposition takes place. When the temper colours are reached, deposition generally occurs, starting at scattered points, which represent cracks in the film. The obvious explanation is that the oxide film continues from the heated end beyond the region of visible temper colours and, although invisible, is sufficiently protective to shield the iron from the copper nitrate solution. At the other extreme, where copper is deposited, the film, if formed at all, is either not thick enough or not continuous enough to protect the metal.

Isolation of the Protective Oxide Film on Iron.

Evans has made a further most important advance by isolating the film at various parts of the metal and rendering it visible even in the parts where it is normally invisible. The film is invisible only so long as it is in optical contact with the

underlying metal and, when removed therefrom, is readily visible if backed by air or a medium such as water, which has no great reflectivity.

The ingenious method of isolation used was to corrode away the metal below the skin either by anodic attack or by treatment with iodine solution, leaving the envelope of oxide film untouched. Not only was Evans able to show by this means that an oxide film is definitely present on the parts of the iron that are " passive " towards copper nitrate solution, but also that there is a ragged film even on the parts which still remain " active." In fact, on exposure to the air, electrolytic iron acquires an oxide film at the ordinary temperature, and if given sufficient time the iron may become passive to copper nitrate without heating. This last fact is of great importance, for it shows not that passive iron is distinguished from active iron by the possession of a film, but rather that any iron which has been exposed to the air acquires an oxide film, which is continuous and *protective* in the case of passive iron, and discontinuous and *non-protective* in the case of the active metal. It also removes a long-standing objection to the oxide-film theory of passivity—the inability of Müller and Koenigsberger (*Physikal. Z.*, 1904, **5,** 413) to distinguish between the reflecting powers of active and passive iron—a matter which has since been cleared up by the work of Freundlich, Patscheke and Zocher, and of Tronstad (see p. 98).

The *anodic method* devised by Evans for isolating the film consisted of trimming the lower edge of a strip of passive iron and clamping vertically in $N/10$-sodium chloride solution so that only the lowest 1 cm. was actually immersed ; the strip was then subjected to gentle anodic treatment, using a current

of 6 milliamps. and taking precautions that the alkali produced at the cathode did not come near the anode.   The early attempts were unsuccessful, probably owing to the presence of a second phase (*e.g.* cementite, Fe_3C) in the metal.   The successful experiments were conducted with a very high-quality electrolytic iron, which had been fused in a vacuum.   Analysis gave carbon 0·04, manganese 0·025, silicon 0·010, sulphur 0·013, phosphorus 0·017, nickel 0·09 per cent.   The main impurity (nickel) would be present in solid solution and would therefore be harmless.

During the anodic treatment, dissolution of the metal started at the bottom, along the trimmed edge where the iron was exposed, and worked upwards, eventually reaching a few millimetres above the water-line.   Examination under a binocular microscope showed that the envelope of the electrode remained intact after the treatment, consisting of two thin, transparent, parallel membranes united at the two edges. The enveloping membrane was ferric oxide and, when freed from adhering metallic particles and tufts of rusty hydroxide, was only pale yellowish-grey by transmitted light.   The envelope preserved in detail the original outline of the specimen, even to showing the marks made by grinding with emery. An improved anodic method is described on page 74.

The *iodine method* of isolating the protective film consisted in scratching a line across the specimen and then immersing it in a saturated solution of iodine in 10 per cent. potassium iodide.   After about two days iodine had corroded the metal almost completely under the scratch, where the iron was exposed, and had penetrated from this region between the oxide film and the underlying metal, so that the transparent skin could easily be removed from the metal below in the form

5

of flakes. Pieces of freshly abraded iron clamped vertically in the iodine solution behaved quite differently; the metal was dissolved completely up to the water-line, but just above the water-line there remained a double, transparent membrane, evidently caused by the iodine solution rising by capillarity and corroding the metal between the two oxide skins produced by the action of the air.

The flakes were 2 or 3 mm. long when freshly removed after the iodine treatment, but broke up into microscopic fragments on washing; they consisted of non-magnetic ferric oxide and were quite transparent; they also showed a tendency to curl into rolls. Viewed under the microscope, the flakes were seen to be covered with a series of lines, which could be made light or dark by altering the conditions of illumination. These lines represent the corrugations left on the surface of the iron by the abrasion with emery, for, when the specimens had been ground in one direction only, the flakes of oxide showed a single set of parallel lines, but when the grinding had been in two directions, two sets of parallel lines intersecting at the corresponding angle were observed. These observations are of importance, because they show quite definitely that the film actually represents the oxidised surface of the original specimen of metal.

The film evidently forms very quickly on iron exposed to the air immediately after grinding. Flakes of oxide were not formed when iron was ground under the surface of the iodine solution, but were produced when specimens were ground with a carborundum disc, held in air for a short time and then plunged into the iodine solution. Even exposure to air for 8 seconds produced a large crop of ragged flakes, and exposure for longer periods gave flakes which became less
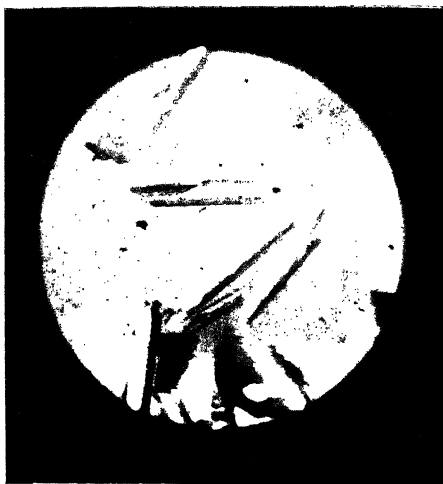
Fig. 6.—Oxide film isolated from heat-tinted iron.

ragged as the exposure increased. These films, produced by exposure to the air at ordinary temperatures for a short time, are not protective. This is probably not due to their extreme thinness, for there is no apparent reason why a uni-molecular film should not be protective under the proper conditions, but is probably due to other causes, which will be discussed in the next section.

Some interesting observations were made on the character of the film isolated from different parts of freshly abraded electrolytic iron, which had been heated in the air at one end to produce a visible scale, the other end remaining cold and apparently unchanged. The iodine method revealed the presence of a transparent, non-magnetic ferric oxide skin on both the apparently unchanged and interference-colour regions. Opaque magnetic scale began to appear below the transparent films as a separate layer about the region of second-order interference colours, and became very thick at the end which had been heated to redness. No sharp change of properties was noticed on passing from the apparently unchanged region to the region of interference colours, a gradual increase of thickness and strength of the film taking place.

In Figs. 6-10 are shown actual photo-micrographs of protective ferric oxide films, which are reproduced through the courtesy of Mr. U. R. Evans. Fig. 6 is not a passivity film, but represents a film isolated from heat-tinted iron, viewed by reflected light, and serves to show the tendency to curl into rolls. The remaining photographs illustrate films isolated by the iodine method from electrolytic iron rendered passive by immersion in potassium chromate solution (see p. 93). These are viewed by transmitted light.

The dark lines are corrugations representing the original

abrasive treatments, but the dark patches are residual metal. Fig. 7 shows the film obtained from iron abraded in two directions at right angles with fine emery flour ; Fig. 8 shows the film from iron abraded in two directions at 45° with coarser emery ; in Fig. 9 the final abrasion was in one direction only, with coarse emery. It will be seen that one film has curled up almost completely ; in Fig. 10 abrasion was in two directions at 90°, with the coarser emery.

The Breakdown of the Protective Film.

The protective properties of the oxide film on iron are most evident over a certain range of thickness, and extremely thin or very thick films are liable to fail. The cracking of the thick film on iron which has been heated in the air is most probably due to compressional stresses set up by the increase of volume involved in the formation of oxide from the metal, but the discontinuity of the extremely thin films formed by exposure to the air at the ordinary temperature appears to be due to quite a different cause. Experiments showed that the time required to produce effective air-passivity to copper nitrate solution increased with the coarseness of the abrasive used. This suggests that the cause of local failure in such films is to be attributed to the internal stresses left by the grinding. When the surface layer of ground iron is converted into oxide, compressional and tensile stresses due to the grinding become available to produce cracking of the surface film. The cracks will be repaired by fresh oxidation, but the repaired film will go on cracking until the internal stresses are sufficiently reduced.

The thickening of the film with time may be due to the passage of oxygen through the open cracks, rather than to

FIG. 7.

FIG. 8.
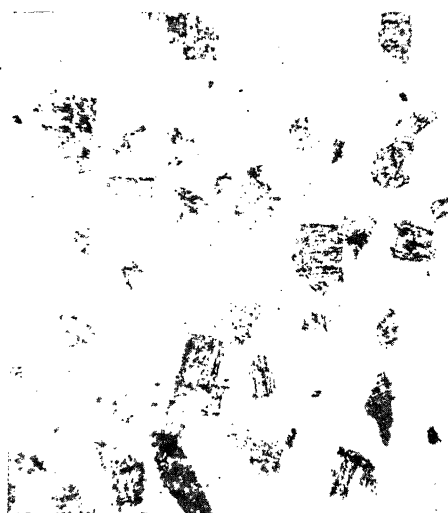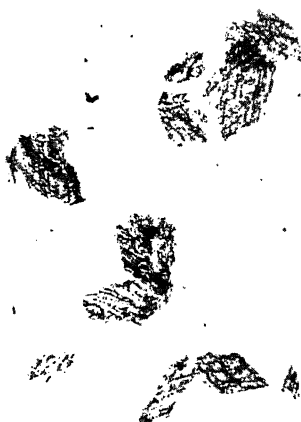
FIG. 9.

FIG. 10.

FIGS. 7-10.—Oxide films isolated from passive electrolytic iron.

[*To face page* 68.

true diffusion of oxygen through the film, a suggestion which is supported by the fact that coarsely-ground iron develops a film of greater thickness than finely-ground iron.

Evans also showed (*J.C.S.*, 1929, 92) that breakdown of the protective film on iron, steel, zinc, or aluminium tends to occur where the specimen has been bent or otherwise distorted. Simple, uniform pressure had no appreciable effect, but the effect was best observed by bending strips of the passive metal and then exposing them to corrosion by dilute solutions of potassium sulphate or chloride. Corrosion occurred preferentially at the bend, and generally more on the convex than the concave side, suggesting that the local attack is due to the cracking of the protective oxide skin. Breakdown of the film is also likely to occur where the surface has been cut or scratched, or where rolling or casting defects occur at the surface of the metal. It is emphasised that internal stresses are important in determining corrosion if they are of such a character as to keep the film in a state of weakness. These conclusions are of particular interest, because, in the first place, they throw a new light on the preferential corrosion of strained metal, which has generally been attributed to a difference in electrolytic solution pressure caused by distortion of the space lattice of the metal; in the second place, they suggest that at least *part* of the acceleration of corrosion by heterophase impurities may be due to the tendency of the protective film to fail at the phase boundary, especially as it is often observed that non-conducting inclusions may determine the sites of corrosion ; and, in the third place, they provide a link between the effects of the differential aeration current and the breakdown of the protective film. Differential aeration currents are ascribed to the differences of potential existing

between the places where the film is kept in repair by the presence of oxygen and those where it is not kept in repair.

The protective film shows a tendency to break down in the presence of solutions of certain electrolytes, particularly those containing small anions, and in solutions there is also a tendency for the film to fail at the water-line, but these effects can be discussed more profitably in Chapter V., where the behaviour in aqueous solutions is considered. The nature of these ions is important, however, in affecting the protective nature of the film either towards corrosion in aqueous solutions or towards atmospheric corrosion.

In the absence of these ions, the film preserves its protective character and the metal does not readily rust, even if it becomes moist. Under favourable atmospheric conditions, therefore, ordinary iron may have a long life without showing signs of serious rusting. Evans ("Corrosion of Metals," 1926, p. 150) refers to metal-work erected at high altitudes on the Italy-Austria frontier for military purposes during 1914-1918, which, when inspected in 1923, was remarkably free from rust. An example which has become fairly well known is an ancient iron column, erected about A.D. 200 at Delhi, which is free from rust, though showing a brown surface tarnish. A sample of this iron rusted readily in the air of an English laboratory (Sir R. Hadfield, *Chem. and Ind.*, 1925, **44**, 1029).

The most important practical benefit of the study of conditions causing the breakdown of the protective film is that light is thrown thereby on the conditions under which the film is permanent. In certain cases, the protective film may be self-healing under widely varying conditions, and this fact is brought into practical use in the applications of stainless steels and other alloys (see Chapter VII.).

The Structure of the Protective Film.

Some very interesting results were obtained by Evans in his microscopical examination of the oxide films responsible for the first-order blue and subsequent tints on iron. When freshly removed, the films sometimes showed holes, and beside the holes, or covering them, were smaller pieces of film usually attached as " flaps " to the main film. The observations suggest that as the relatively thick films crack, oxygen gains access to the exposed metal below the crack and produces a patch-work of repairs. This also accounts for the observation that the thicknesses of different flakes taken from the same area of the specimen show a considerable variation ; if, after the iodine treatment, the patch remains adherent to the first film, a local thickening will be visible at the site of the crack, but, if it does not adhere, a separate specimen of the patch formed by the repair will be obtained, and this will be thinner in general than the average thickness of the film.

The question of the thickness of the film is a difficult one. It is probable that the film on a perfectly smooth iron surface is only a few molecules thick, or even unimolecular, but such films cannot be separated from the underlying metal. The oxide films which have been removed from coarsely-ground metal appear to be relatively thick from the molecular point of view, probably because the oxygen has penetrated up into cracks, and the difficulty is increased by the corrugation of the film. Apart from this, in general, the film isolated consists of a mixture of oxide and metal. Sometimes it is almost entirely oxide and is then transparent, with a few opaque inclusions of metal ; at other times, particularly in the thinner films, it is largely metal and is then mainly opaque, with " windows," representing portions occupied entirely by the oxide film. In the

thinnest films, much residual metal is usually present and the film, which seems almost incapable of existing without the stronger support of the metal, tends to shrivel around the places where the inclusions of iron are present.   All the evidence points to the interlocking of oxide and metal.

The structure of the surface film has been further elucidated by the work of U. R. Evans and J. Stockdale (*J.C.S.*, 1929, 2651). Fig. 11 * gives a representation of the surface of a metal which has been exposed to the air.   F. P. Bowden and E. K. Rideal
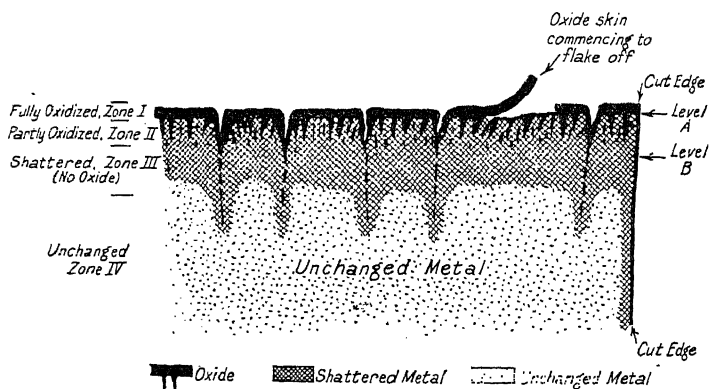
FIG. 11.—Oxidised surface of a metal.

(*Proc. Roy. Soc.*, 1928, **A.**, **120,** 59 ;   *Nature*, 1928, **122,** 647) have found that the true surface area of metals greatly exceeds the apparent area, especially after abrasion, the surface probably containing invisible fissures, up which oxygen can penetrate to a certain distance.   Where the fissures have become so narrow as to be comparable with atomic dimensions, the material may be regarded as shattered metal, having a distorted lattice. Such material will be more unstable and more readily corroded than the unchanged metal below.   Near the mouths of the

* Reproduced by kind permission of Mr. Evans and the Council of the Chemical Society.

fissures, where an oxide film has been able to form, the material will be less corrodible than the unchanged metal. Evans and Stockdale describe the four zones represented in Fig. 11 thus : " (1) An outer zone, consisting *wholly of oxide ;* (2) a zone containing *oxide and metal*, the proportion of metal gradually increasing as one passes inwards—this zone should have an abnormally *high resistance to attack ;* (3) a shattered zone, *fairly free from oxide*, and having an abnormally *low resistance to attack ;* (4) the *unchanged metal*, forming the main interior portion."

At low temperatures, oxygen will penetrate below the oxide film mainly through the fissures, whilst with rising temperature diffusion through the film becomes more rapid and Zone I. gradually thickens at the expense of Zone II. and finally of Zone III. It appears that the method of removing the film with iodine depends on preferential dissolution along Zone III., but a good deal of the unchanged metal in Zone II. is also dissolved by the iodine.

Evans and Stockdale have devised an improved electrolytic method of isolating the film, by dissolving away Zone III. The residual metal in Zone II. is thereby preserved, because dissolution of the metal particles ceases when they are out of electrical contact. The older anodic method works well with pure, electrolytic iron which is very thin, but the improved method can be used for iron of any thickness, and high purity does not seem to be necessary, since passivity films have been stripped by its means from steel with 0·18 per cent. of carbon, although the method failed with steel containing 0·26 per cent. of carbon and 0·15 per cent. of silicon. Further, since the actual electrolysis can be conducted below an atmosphere of hydrogen, there is no production of ferric salts and the films

are quite free from " rust " or secondary hydroxide, such as may be produced by the hydrolysis of ferric salts. Thus, the method gives cleaner films than are obtained by the iodine method, and is more widely applicable than the older anodic method. The procedure is an important practical development and has been adapted for quantitative purposes, and the following description, as applied to iron, is quoted from the paper of Evans and Stockdale. (See Fig. 12.)
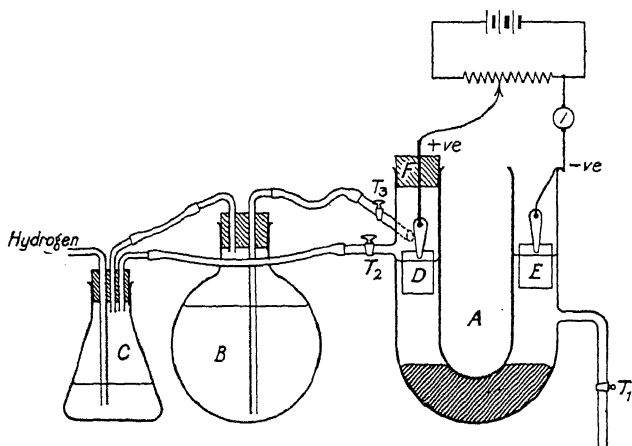
FIG. 12.—Apparatus for isolating the protective film.

" The U-tube (A) had three side-tubes, fitted with taps. Tap T_3 led to a 3-litre reservoir B (not drawn to scale) containing air-free water, which was connected, through flask C containing dilute soda, to a Kipp's hydrogen generator. The tap T_2 connected the U-tube direct to C, and tap T_1 was used to control the washing process. The anode D was held in place by a metal clip soldered to a stout copper wire making a tight fit in the rubber stopper F, whilst the cathode E hung loosely from the side of the cathodic limb ; the electrodes were connected through an ammeter and rheostat as shown. The procedure during an experiment was as follows :

"The taps T_1, T_2, and T_3 are closed; the U-tube is filled with electrolyte to the required level, and a few crystals of ferrous sulphate are dropped into the solution in the cathodic limb. The ferrous solution so produced serves to take up the alkali as soon as it is formed during electrolysis, and confines precipitation to a small zone round the cathode and above the opening of the exit tube. The mouth of the cathodic limb is made temporarily airtight by fitting it with a rubber stopper, and the tap T_2 opened to allow a brisk flow of hydrogen to displace the air in the anodic limb ; while T_2 is still open, the stopper F, with the specimen attached, is placed in position. T_2 is then closed, the stopper in the cathodic limb is replaced by the cathode, and the necessary electrical connexions are made. When anodic treatment is finished, the cathode is again replaced by a stopper, and the tap T_3 is opened. (The back surface of the anode is protected by nitrocellulose varnish, and the wash-water inlet, shown dotted, is placed opposite this surface, so that eddies due to the flow of water are checked by the anode itself, thus minimising the risk of breaking the film.) The wash-water in B is under pressure from the Kipp's apparatus, and its rate of flow into the U-tube is controlled by the tap T_1. When washing is complete, tap T_3 is closed and the anode removed carefully. The film is stripped by washing the anode gently with a jet of boiling water or by swirling it in freshly boiled water. The flakes so obtained are dissolved immediately, under an atmosphere of carbon dioxide, in the requisite quantity of hydrochloric acid ; this quantity is governed by the approximate thickness of the film and the acidity of the standard solution against which it is to be matched by the thiocyanate method."

In order to ascertain whether reasonably thorough washing

of soluble iron salt from the flakes was possible, the following experiment was performed. A nickel anode with its film previously loosened, but clinging, was introduced into the U-tube of the apparatus just described after the operation of separating an iron film. The nickel film was then washed, removed, dissolved, and the resulting solution tested for iron ; the iron found was not appreciably greater than in a blank experiment, the small amount present being derived as an impurity from the nickel.

Applied to iron, heat-tinted to the first-order yellow, the method enabled two distinct types of flake to be obtained. The edges were freshly trimmed before the experiment, so as to allow the anodic attack at Zone III.; the flakes obtained were fairly thick and contained residual metal. The ferric oxide content of these flakes was determined to be about 5×10^{-5} grm. per sq. cm. On the other hand, if the edges of the specimens were protected, anodic attack starting at local failures in the film, the films isolated were thinner, more transparent, and practically free from residual metal. These flakes consisted almost entirely of oxide, giving a value of about 2×10^{-5} grm. per sq. cm., in agreement with Constable's optical determination of the thickness of the film on yellow-tinted iron, viz. 0.46×10^{-5} cm. or 2·36 grm. per sq. cm. (*Proc. Roy. Soc.*, 1928, **A., 117,** 376). This thin type of film is liberated by the anodic attack spreading along the boundary of Zones I. and II.

Some observations with nickel are interesting. In some cases it was possible to transfer the loosened film on to a glass surface, previously covered with a nitrocellulose varnish which had been allowed to dry sufficiently to reach a " tacky " condition. The electrode, with its clinging, but undermined film, was simply pressed against the nitrocellulose surface,

whereupon the loosened film left the metal, being transferred to the prepared surface, and could be washed and dried. The variation in thickness of the film removed from a strip of metal, which had been heated at one end, could then be easily observed. In a private communication, Mr. Evans has informed the author that it has since been found better to transfer the film to cellophane rather than to glass ; the flexibility of the cellophane is an advantage and the colours of the transferred film (nearly complementary to those on the metal) show up well if the cellophane is then mounted on a dark background, preferably with nitrocellulose adhesive filling the space between the cellophane and the black paper.

Many of the oxide films isolated from nickel were remarkably free from metallic inclusions, whilst the films removed from copper, like those from iron, gave evidence of the interlocking of metal and oxide. The films removed from some varieties of nickel have, however, been found to contain a considerable amount of residual metal. Whether interlocking occurs or not in the thinner oxide films appears to depend largely on the previous mechanical treatment of the metal.

Optical and Other Evidence.

H. Freundlich, G. Patscheke, and H. Zocher (Z. physikal. Chem., 1927, 130, 289) prepared mirrors of pure iron by the thermal decomposition of iron pentacarbonyl in the complete absence of oxygen. The reflecting power of these mirrors was measured and was observed to fall suddenly when oxygen was admitted. Simultaneously the chemical activity of the iron was reduced. The observations are consistent with the formation of an oxide film at the surface of iron on the admission of air.

Application of X-ray and other methods has so far proved of little help. F. Krüger and E. Nähring (*Ann. Physik.* 1927, **84,** 939) obtained identical X-ray spectrograms for active and passive iron, nickel, and chromium in the finely-divided condition, and failed to observe any extra lines due to the oxides. The absence of shift in the lines proper to the metals indicated no distortion of the space lattice, and the authors considered that their evidence showed that films of oxide on these metals were not thicker than 10^{-7} cm. As Evans pointed out (*Nature,* 1928, **121,** 351), the small particles of metal used, being free from strain, would be free from cracks in the film and films obtained under these conditions would be exceedingly thin. There is no reason to suppose that a protective film need exceed 10^{-7} cm. in thickness, provided that it is really continuous. Vernon's observations on copper (p. 55) suggest that even a unimolecular film may be protective.

A criticism of the X-ray method of investigation is that there is no reason to suppose that the film has a crystalline space-lattice. A film of the dimensions believed to exist on passive metals may conceivably be amorphous ; indeed, its gradual crystallisation may be a cause of the breakdown of passivity.

G. P. Thomson (*Proc. Roy. Soc.*, 1930, **A., 128,** 649), applying his method of electron diffraction to the analysis of surface layers has studied the surface of iron after immersion in concentrated nitric acid. No difference in the diffraction patterns of active and passive iron was observed, and it was concluded that if a surface layer of oxide is present it must be exceedingly thin. It should be pointed out that both aluminium, covered with the usual film which forms in air, and lead, freshly cut and heated in air at about 100° C. for some

time, gave no diffraction pattern. This method, whilst providing a promising line of attack in the investigation of the structure of surface layers, replacing the too highly-penetrating X-ray by the softer electron, cannot yet be held to have given any definite evidence of the nature of the passive layer on metals.

So far as it goes, the X-ray and electron diffraction evidence rather suggests that the protective oxide film is amorphous, although it is too early to pronounce a definite view. The work of Kohlschütter and Krähenbuhl (*Z. Elektrochem.*, 1923, **29,** 570) on silver halide films suggest that these do not attain their proper crystalline structure until they reach a considerable thickness.

CHAPTER IV.

PROTECTIVE FILMS FORMED DURING ATMOSPHERIC CORROSION.

A GREAT proportion of the metal-work used throughout the world is normally exposed to the atmosphere, and it happens that metal structures are mostly required in industrial centres, where the air suffers from pollution by a variety of gases and finely-divided liquid and solid particles. The ravages of rusting are often combated by plating the metal with a thin film of some less corrodible metal, but the efficacy of this treatment in turn generally depends on the formation of a highly protective film of oxide or other compound, so thin as to be invisible, on the surface of the plating metal. The formation of more or less protecting films by the action of different types of atmospheres on various metals is, therefore, a study of very great importance. Wherever a satisfactory protective film is acquired spontaneously through the process of corrosion, the need of artificial protection is reduced, or vanishes. Some spontaneously acquired films are not suitable for the conditions of employment of the metal, but in some cases they may even add to the æsthetic value. For example, the invisible oxide film formed at a surface of polished chromium does not diminish for practical purposes the highly reflective properties of the metal, and the green patina, which forms on copper under some conditions, not only affords protection from further atmospheric corrosion, but has also an æsthetic value.

Important observations on the formation of protective films of this type are embodied in the First and Second Experimental Reports to the Atmospheric Corrosion Research Committee of the British Non-Ferrous Metals Research Association (W. H. J. Vernon, *Trans. Faraday Soc.*, 1924, **19**, 839 ; 1927, **23**, 117). Vernon examined the initial *tarnishing* of a number of metals exposed to different types of atmospheres, by measuring both the *increase of weight* of the metal and its loss of reflectivity. During the initial stages of atmospheric corrosion, the product remains *in situ* and the specimen *increases* in weight. Vernon follows J. N. Friend (*Carnegie Schol. Mem.*, 1922, **11**, 1) in applying the term " surrosion " to denote this kind of corrosion. The types of atmosphere investigated were (1) an indoor atmosphere maintained continuously unsaturated with water vapour, (2) an indoor atmosphere of variable (but relatively high) humidity, occasionally reaching saturation, (3) the atmosphere of an ordinary domestic kitchen, (4) open-air exposure at South Kensington.

Before discussing some of the results obtained with individual metals, reference must be made to an important aspect of the research, which is concerned with the relation between weight-increment and time for indoor atmospheres. Four types of curve have been distinguished :—

(1) A *parabola*, the axis of which coincides with the *time-axis* of the co-ordinates. In this case, the weight-increment is evidently proportional to the square root of the time, the rate of growth of the film being regulated by the rate of diffusion of the corroding atmosphere through the tarnish-film. This type of film is *protective*. *Example :* Copper, within a wide range of humidity conditions.

(2) A *straight line*. In this case, the weight-increment is

proportional to the time and the film does not impede the course of corrosion. This type of curve indicates the formation of a *non-protective* film. *Example :* Zinc. There is evidence, however, of a short initial period during which the linear relation does not hold. Thus, the straight line which persists from the first day's exposure onwards cuts the vertical axis a little above the origin, indicating a greater initial rate of attack, which quickly assumes a lower and constant value.

(3) A *parabola*, the axis of which coincides with the *weight-axis* of the co-ordinates. In this case, the weight-increment is proportional to the square of the time. The rate of attack increases with the duration of exposure. The scale is discontinuous, and accelerates the attack on the remaining metal in proportion to the amount which is already present. *Example :* Iron in an atmosphere of relatively high humidity, intermittently reaching saturation.

(4) A curve, similar in type to that representing velocity of adsorption, beginning with a resemblance to a parabola and quickly flattening towards the horizontal axis. The curve does not appear to be capable of representation by a simple mathematical function. This type of curve was obtained with aluminium and lead, and indicates a highly *protective* film.

An interesting feature of curves (1) and (2) is that they correspond with the types of curves recognised by Pilling and Bedworth (see p. 52) for oxidation at high temperatures, and experimentally verified by them for copper, cadmium, and magnesium.

Tarnishing of Copper.

The tarnishing of copper in indoor atmospheres is due mainly to the presence of gaseous sulphur compounds, and

air which is free from such compounds has no visible effect on copper, although the formation of an invisible oxide film can be demonstrated.   Air which has been filtered over silver does not tarnish copper.   At the same time, the tarnish film contains only about 6 to 9 per cent. of sulphide, the remainder being assumed to be oxide.   When the concentration of reactive sulphur corresponds to about one volume of hydrogen sulphide in 35,000,000 volumes of air (a condition approximating to town-air in winter), tarnishing of copper is comparatively rapid and gives a purplish surface in the course of a week or two, but tarnishing ceases when the concentration of reactive sulphur falls below one volume in 600,000,000 volumes of air (a condition approximating to suburban atmospheres during summer).

An important feature of the weight-increment curves obtained for copper tarnishing in an ordinary indoor atmosphere is that the points fall on a parabola independently of wide changes in the sulphur content of the atmosphere during the exposure.   The conclusion follows that the process is controlled entirely by the properties of the initially-formed film. When copper is first exposed during the summer period tarnishing in the indoor atmosphere does not occur, and when winter comes the curve still continues its original course and the metal remains untarnished ;   on the other hand, copper which is first exposed during the winter months (relatively high concentration of sulphur) tarnishes very quickly.   These results show that the practically invisible film, which forms during the non-tarnishing period, actually confers immunity from tarnishing upon the underlying metal, and recall the experiments of Vernon (p. 55) on the effect of gently heating copper in the air.

Evidently there is a great difference between the protective properties of the pure oxide film formed in an unpolluted atmosphere, and the film consisting of a mixture of oxide and sulphide formed in a polluted atmosphere, which is permeable to sulphur compounds, allowing further tarnishing to proceed. The difference is believed to lie in the original space lattice of the two types of film.   A lattice in which sulphur does not appear may be expected to resist the intrusion of sulphur atoms more than a lattice containing copper, oxygen, and sulphur atoms.

Pure sulphide films, formed by exposure to hydrogen sulphide, were found to be relatively permeable to both oxygen and sulphur compounds, and actually to be more rapidly attacked than untreated copper.   As Vernon points out, this observation has an important bearing in metal colouring and indicates that preference should be given to oxide films rather than to sulphide films.

Vernon reports some interesting experiments carried out by L. Whitby on the effect of smoke on a clean copper surface. Exposure to the smoke from tobacco, cotton wool, or paper, whilst producing practically no visible change in the metal, rendered it immune to tarnishing under atmospheric conditions which tarnished ordinary copper.   Similar observations were made with silver.

Tarnishing of Zinc.

The linear relation between the weight-increment and time in the tarnishing of zinc suggests that the film owes its non-protective character to a discontinuous structure, oxygen diffusing through the interstices between the scales of oxide. This view has been confirmed by microscopical observations.

Another consequence of such a granular structure is that any colour effects of the film will be due to diffraction, rather than to interference, and the appearance of a blue tint on zinc, without passing through the usual sequence of interference colours, supports this supposition. According to W. S. Patterson (*J. Soc. Chem. Ind.*, 1931, **50**, 120 T) the deposit formed on zinc during outdoor corrosion in an urban atmosphere does not offer complete protection to the metal, but nevertheless has a retarding effect on the rate of corrosion.

Tarnishing of Brass.

Whilst copper gives a parabolic and zinc a linear weight-increment curve with time, brass (70/30 and 60/40) gives a mixed type of weight-increment curve, as might be expected. In its early portion the curve is parabolic and gradually merges into a straight line, suggesting that the copper constituent is the predominating factor at first, whilst later the zinc assumes the control. This conclusion has been confirmed by microscopical examination of the film on 60/40 brass, for in the early stages the attack is confined mainly on the α constituent (rich in copper) and the film is of the continuous type, as observed on copper ; later, the attack becomes concentrated on the β constituent (rich in zinc) and the product is then of the discontinuous type, as observed on zinc.

Films produced by the oxidation of brass in air cannot be expected, therefore, to have a degree of protection comparable with that of the film on copper. This is found to be true in practice.

Tarnishing of Aluminium.

Reference has already been made to the peculiarity of the weight-increment curve for aluminium, which, whilst starting

in an almost parabolic form, rapidly flattens towards the time axis and becomes practically horizontal after about ten days, the thickness of the film then being about a millionth of a centimetre. Obviously this is an extremely favourable type of protective film, which excludes the corrosive atmosphere completely, any further corrosion being due to cracks in the film. Probably, the growth of the film does not depend on diffusion at all, but on adsorption, a view which is consistent with the type of curve obtained and with the extreme thinness of the film.

Measurements of the increase of weight during exposure up to the horizontal part of the curve gave an average value of 0·19 mg. per sq. dm., and from this result the thickness of the film can readily be calculated, knowing the density of the oxide. The exact composition of the film formed by atmospheric corrosion is not known, but it may be supposed to lie between Al_2O_3 and the commonest hydrated oxide, $Al_2O_3, 2H_2O$, the densities of which are, respectively, 3·9 and 2·55. A simple calculation shows that, assuming the density of the film to be 3·9, the thickness of the film is $1·04 \times 10^{-6}$ cm. and, assuming it to be 2·55, the thickness is $1·35 \times 10^{-6}$.

Tarnishing of Lead.

The relation between weight-increment and time in the corrosion of lead is similar to that described for aluminium. The increase of weight on reaching the nearly flat portion of the curve, for which a period of about seven days is required is about 0·10 to 0·15 mg. per sq. dm., as compared with 0·14 to 0·24 mg. per sq. dm. for aluminium. From these data it is difficult to calculate the thickness of the film, because one cannot be sure which oxide of lead is formed, but it appears

that the film is of the same order of thickness as that on aluminium.

Vernon describes a most interesting effect of the vapour of turpentine (presumably) on the corrosion of freshly-cleaned specimens of lead. Freshly-cleaned sheets of lead, exposed in a room near which painting was in progress, gained in weight very rapidly and assumed a deep blue colour. Other metals similarly exposed suffered no change. From the present point of view, the chief interest of these observations is that lead which had previously been exposed to relatively pure air suffered no change when the painting operations in the building started. The behaviour is illustrated in a striking way by Fig. 13, which is reproduced from Vernon's paper.* Curve A represents the mean weight-increment of two specimens first exposed on 1st April, 1925. Curve B represents, to the same scale and in its correct chronological position (commencing 13th August, 1925), the attack upon specimens during the tarnishing period.

Apart from the enormously greater rate of oxidation indicated by curve B, it will be observed that curve A, in spite of the smallness of the ordinates, passes through the tarnishing period without suffering the slightest deflection. A more convincing example of the practical value of protection afforded by an excessively thin film of oxide can scarcely be desired. Another point of interest is that, as in the parallel case of copper in the presence of gaseous sulphur compounds, here again the production of a non-protective type of film is determined by the presence of a small concentration of a foreign constituent in the atmosphere. Evidently the foreign constituent, if

* By kind permission of Dr. Vernon and the Council of the Faraday Society.

present at the time of formation of the film, produces a small difference in the structure of the oxide film, which serves
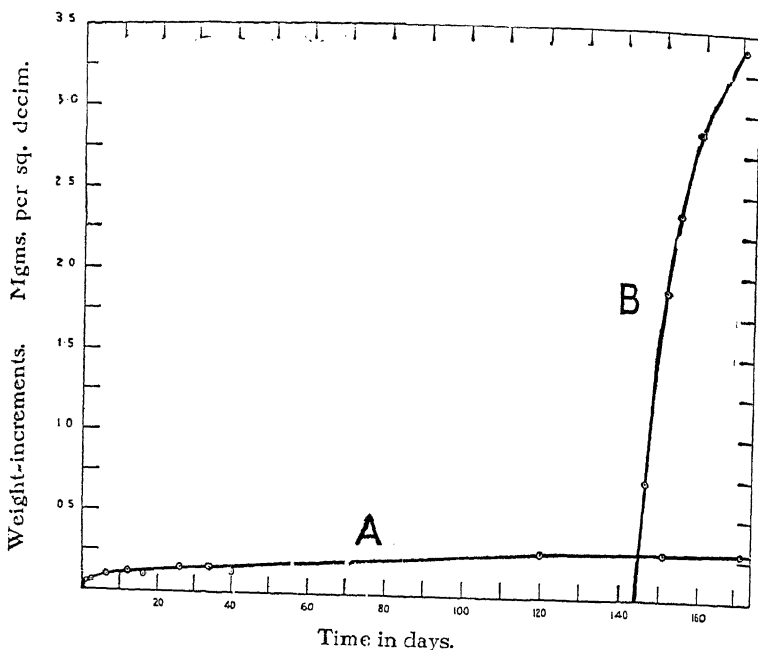
FIG. 13.—Rate of tarnishing of lead.

to keep it permeable. On the other hand, if the oxide film is completed in the absence of the foreign constituent, it is impermeable to the latter when it is presented.

Tarnishing of Iron.

In an unsaturated atmosphere, below a certain critical humidity (in the neighbourhood of 70 per cent. relative humidity), the weight-increment curve for iron is concave towards the time axis, the rate of attack thus falling off with increasing time. Above the critical humidity an enormous increase in corrosion rate occurs in iron which has previously rusted

below the critical humidity.   In a humid atmosphere inter-
mittently reaching saturation, the weight-increment curve is
concave towards the weight axis, the rate of corrosion increasing
with increasing time.   A wide range of corrosion types may
thus be encountered according to the external conditions.   The
behaviour of iron is fundamentally different from that of the
non-ferrous metals, the rust being discontinuous from the
start, occurring in isolated spots, which gradually increase in
number and size.

Rusting of iron does not occur above the dew-point if all
suspended matter is removed from the air by filtering, or even
by shielding the specimen by a single thickness of muslin.
In such a case, ordinary iron develops a protective oxide film,
as may be shown by subsequent exposure of the specimen
together with a piece of freshly cleaned iron ;   the freshly
cleaned specimen proceeds to rust, whilst, for an appreciable
time, the pre-exposed specimen remains bright.

The Surface Patina on Copper Exposed to Open-Air Corrosion.

W. H. J. Vernon and L. Whitby (*J. Inst. Metals*, 1929, **42**,
181 ; 1930, **44**, 389) have made a study of the green patina
which forms on the surface of exposed copper in various types
of atmosphere.   Some of the specimens were very old, being
taken from the roofs of buildings.   Contrary to the general
belief that the patina consists of basic copper carbonate, it was
shown that it is mainly basic copper sulphate ;   it is interesting
to note that in course of time the composition of this constituent
shows complete agreement with that of the mineral brochantite,
$CuSO_4, 3Cu(OH)_2$.   The patina may be largely basic copper
chloride in seaside districts, but when urban and marine

conditions coincide the basic sulphate predominates in the product. The sulphate is obtained from sulphurous and sulphuric acids brought into the atmosphere through the combustion of coal. In urban atmospheres, the metal passes through a preliminary black stage for a period of some years and the green patina appears to be better developed at relatively high altitudes ; a good example of this is the green copper dome on the Alexandra Tower of the Imperial Institute, South Kensington, which is about 300 feet above the level of the street.

The specimens of copper examined were remarkably free from pitting, and there appears to be no doubt that the longevity of copper exposed to the atmosphere is due to the protective properties of the film of basic sulphate. A. N. Cathcart (Discussion, *ibid.*, p. 197) states that the thickness of the copper roof of the Bodleian Library at the present day is practically the same as when it was first laid, in 1830, thus showing that there has been no appreciable loss of metal during one hundred years' exposure. As a development of this work, a patent has recently been taken out for an artificial coating of basic sulphate for copper intended for outdoor exposure (see p. 186).

CHAPTER V.

PROTECTIVE FILMS FORMED IN LIQUID MEDIA.

THE principal factors determining the corrosion of metals in aqueous solutions are the solution tension of the metal and the physical and chemical properties of the product. Given a solution tension such that the reaction will start, how far it will proceed will depend to a large extent on the solubility of the product. If readily soluble, there is no reason why the reaction should not continue rapidly, as in the dissolution of zinc in dilute sulphuric acid or of aluminium in sodium hydroxide solution. If the product is insoluble, it may or may not allow further corrosion, depending on whether its physical properties are such as lead to a sufficiently protective film.

An example of an insoluble product which is useless as a protective agent is furnished by the reaction of tin with concentrated nitric acid. The reaction is violent and produces a voluminous mass of hydrated stannic oxide. It is probable that if this same oxide were produced as a compact mass undergoing little change of volume, the first film produced would protect the rest of the metal from further attack. All the conditions are right for a true passivity except the physical properties of the oxide as produced under these conditions.

protection against corrosion in liquid media is when that product is not produced primarily in the reaction, but by a secondary process. An excellent example is in the ordinary rusting of iron or in its corrosion in a solution of sodium chloride. In the latter case alkali develops at the cathodic parts of the metal and ferrous chloride at the adjacent anodic parts, and where these two solutions meet ferrous hydroxide and eventually ferric hydroxide is the product. A deposit of rust formed in this way cannot be expected to have protective properties, for the particles of hydroxide are formed out in the solution and have little real contact with the metal. The supposition is confirmed by the experiments of G. D. Bengough, J. M. Stuart, and A. R. Lee (*Proc. Roy. Soc.*, 1927, **A., 116,** 451 ; 1928, **A., 121,** 88 ; 1930, **A., 127,** 42), and those of G. D. Bengough, A. R. Lee, and F. Wormwell (*ibid.*, 1931, **A., 131,** 494 ; 1931, **A., 134,** 308), who have found that the rate of corrosion of pure zinc and iron in dilute solutions of potassium chloride and sulphate in the presence of oxygen is influenced very little by the accumulation of the corrosion products, even over a period of 100 days. This has been shown strikingly in the case of specimens which during their immersion have accumulated a relatively thick, mossy overgrowth of rust. The specimens continue to corrode at the same rate after removal of the overgrowth.

A different state of affairs is shown in the measurements of R. H. Brown, B. E. Roetheli, and H. O. Forrest (*Ind. Eng. Chem.*, 1931, **23,** 350-352) on the *initial* corrosion rates of metals in oxygenated water. These were measured by rotating an oxide-free metal cylinder in oxygenated water and determining the decrease of oxygen concentration during the test.

in the order: aluminium, zinc, iron, copper, nickel, tin, silver. The rate of corrosion of the first three metals appears to depend on the rate of diffusion of oxygen to the specimen, but with the others the rate of oxidation of the metal is the controlling factor. The initial corrosion rates of all the metals decrease after a relatively short time, indicating the formation of partially or completely protective films in all cases.

There are numerous reactions in which the direct product of reaction is insoluble in the corroding medium ; thus the resistance of lead to sulphuric acid is a fact utilised in the manufacture of sulphuric acid. Other reactions include the slow dissolution of several metals in concentrated sulphuric acid whilst freely dissolving in the dilute acid. The sulphate of the metal is in many cases insoluble or soluble to a relatively small degree in the concentrated acid. This type of protection calls for no further comment. The most interesting case, however, is the passivity induced in iron and to a certain extent in some other metals by exposure to certain solutions with oxidising properties. The subject is particularly interesting at the present time because, although it has been controversial for almost a century, it has lately come to be almost completely understood.

The Action of Neutral Oxidising Solutions on Metals.

It has been known for a long time that iron, after having been immersed in an oxidising solution such as potassium chromate, potassium permanganate, or hydrogen peroxide, is rendered relatively inert or passive, no longer receiving an immediate deposit of copper when placed in a solution of copper nitrate. The effect is similar to if not identical with that

Whilst the oxidising properties of the solutions involved have suggested that the iron owes its inertness to the acquisition of a film of oxide, there have been at times more or less weighty arguments against this view. The formation of such a film in the case of immersion in solutions of potassium chromate has been demonstrated directly by U. R. Evans (*J.C.S.*, 1927, 1031), who has isolated the film by methods similar to those described in Chapter III. In the case of electrolytic iron it appears that the main function of the potassium chromate is to repair the discontinuities in the oxide film already produced by the action of the air, but in addition there is some evidence that the chromate causes thickening of the film.

Some experiments on similar lines were carried out with aluminium. Although, when freshly abraded or rendered active by immersion in sodium hydroxide solution, aluminium was quickly attacked by iodine solution, after seventy minutes immersion in $M/20$-potassium chromate it reacted only very slowly. Undermining of the surface layers then gave transparent flakes of oxide containing opaque areas due to residual metal.

Strips of copper which had been immersed in $M/20$-potassium chromate solution yielded on anodic treatment a skeleton containing some flakes of transparent cupric oxide, appearing bluish-grey by reflected light, some of which showed signs of the original abrasion with emery. It appeared that this film of transparent oxide lacked mechanical strength.

W. H. J. Vernon (*Trans. Faraday Soc.*, 1927, **23**, 120) has shown that specimens of copper cleaned with chromic acid solutions are remarkably resistant to tarnishing on subsequent exposure to the atmosphere. E. A. Bolton (*J. Inst. Metals*,

The Action of Concentrated Nitric Acid on Iron.

That iron becomes chemically inert or passive when immersed in concentrated nitric acid was observed as early as 1790 by Keir (*Phil. Trans.*, 1790, **80**, 359). A historical survey of early observations of the phenomenon has been compiled by Heathcote (*J. Soc. Chem. Ind.*, 1907, **26**, 899), but some views expressed by Faraday (*Phil. Mag.*, 1836, **9**, 57, 122 ; 1837, **10**, 172) a century ago appear so striking in the light of recent research that they deserve attention here.

It was already known that iron, made passive by immersing in concentrated nitric acid, was no longer dissolved by nitric acid of d 1·35 and failed to precipitate copper or silver from their solutions. Faraday's attention was directed to the phenomenon by a letter received from Schönbein, dated 17th May, 1836 (published in *Phil. Mag.*, 1836, **9**, 53). A month later, Faraday sent a communication to the Philosophical Magazine in which he explained this " peculiar state " of iron. The explanation appears to have been influenced by Schönbein's observation that iron was made indifferent to nitric acid of d 1·35 either by oxidising the metal by heating in the air or by previous immersion in more concentrated nitric acid, suggesting that concentrated nitric acid has some oxidising action on the metal.

Faraday writes : " My strong impression is that the surface of the iron is oxidised, or that the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation ; and that having thus their affinity for oxygen satisfied, and not being dissolved by the acid under the circumstances, there is no renewal of the metallic surface, no reiteration of the attraction of successive particles

electrolyte, and therefore not those successive chemical actions by which the electric current (which is definite in its production as well as in its action) can be continued."

In the light of the work described in Chapter III. on the formation of oxide films by heating metals in the air, the following remarks of Faraday are striking: " In support of this view . . . it cannot be doubted that the formation of a coat of oxide over the iron when heated is the cause of its peculiar and inactive state : the coat of oxide is visible by its colour. In the next place, all the forms of experiment by which this iron, or platina, or charcoal, or other voltaic arrangements are used to bring ordinary iron into the peculiar state, are accompanied by a determination of oxygen to the surface of the iron. . . . That the coat of oxide produced by common means might be so thin as not to be sensible and yet be effectual, was shown by heating a piece of iron an inch or two from the end, so that though blue at the heated part, the end did not seem in the slightest degree affected, and yet that end was in the peculiar state."

It was objected that an oxide film should be dissolved by the acid and could not therefore form a protective film, and this objection has been raised from time to time since. As the subsequent pages of the present chapter show, it has now been demonstrated that iron remains passive under conditions such that freshly ignited ferric oxide is insoluble and becomes active when the dissolution of ferric oxide becomes appreciable. Faraday's views on this problem are contained in the following excerpt from his paper :—

" Why the superficial film of oxide which I suppose to be formed when the iron is brought into the peculiar state by voltaic association, or occasionally by immersion alone into

nitric acid, is not dissolved by the acid, is, I presume, dependent upon the peculiarities of this oxide and of nitric acid of the strength required for these experiments ; but as a matter of fact it is well known that the oxide produced upon the surface of iron by heat, and showing itself by various colours, is scarcely touched by nitric acid of the given strength though left in contact with it for days together. That this does not depend upon the film having any great thickness, but upon its peculiar condition, is rendered probable from the fact that iron oxidised by heat, only in that slight degree as to offer no difference to the eye, has been left in nitric acid of the given strength for weeks together without any change."

Although solid foundations were thus laid for the protective oxide-film theory of passivity almost a hundred years ago, the theory did not gain general approval until recent times. The reason was largely because chemists regarded with disfavour the view that a thin film of oxide could be stable in acid solution, but, as the following pages show, this objection is due to a misapprehension. The obvious alternative explanation was that the iron or other metal is transformed into an inert allotropic modification when it becomes passive and therefore behaves as a noble metal. Such views were expressed by J. J. Berzelius (*Lehrbuch der Chemie*, 5 Aufl., **2**, 699, Dresden and Leipzig, 1844) and by Hittorf (*Z. physikal. Chem.*, 1898, **25**, 729 ; 1899, **30**, 481 ; 1900 **34**, 385 ; *Z. Elektrochem.*, 1900, **7**, 168), and gained a considerable body of supporters. In more recent times the theory has been revived in an electronic form by A. Smits (" Theory of Allotropy," 1922), and W. J. Müller, whilst admitting the reality of the Evans film as an explanation of the phenomena of air-passivity, still maintains that the passivity of metals produced by anodic

polarisation involves an essential change in the state of the metal (see Chapter VI.).

During the last few years the production of protective oxide or similar films has come to be regarded almost universally as the true cause of all types of passivity, as a result of the researches described in the following pages.

An argument which at one time seriously opposed the oxide-film theory was based on the failure of Müller and Koenigsberger (*Physikal. Z.*, 1904, **5,** 413 ; 1905, **6,** 847) to distinguish between the reflecting powers of active and passive iron.   Haber and Goldschmidt (*Z. Elektrochem.*, 1906, **12,** 64) pointed out that active iron might also have an oxide film which was non-protective and discontinuous, in which case a difference in reflecting power could not be expected. Passivity is thereby ascribed not so much to the possession of a film, but to the freedom of a film from porosity.   The observations of Evans (p. 64), that any iron which has been exposed to the air acquires an oxide film, which is continuous and protective in the case of passive iron and discontinuous and non-protective in the case of the active metal, went a long way towards annulling the objections of Müller and Koenigsberger. The objection was finally removed by H. Freundlich, G. Patscheke, and H. Zocher (*Z. physikal. Chem.*, 1927, **130,** 289), who prepared mirrors of iron free from oxide by decomposing iron pentacarbonyl by heating in the absence of air.   When air was admitted, a fall in the reflecting power of the mirrors was observed and the chemical reactivity of the iron was reduced simultaneously.

In another paper Freundlich, Patscheke, and Zocher (*Z. physikal. Chem.*, 1927, **128,** 321) describe some very interesting observations on the behaviour of these mirrors of pure iron

towards concentrated nitric acid. A difference of behaviour was noted accordingly as the mirror had been prepared in the complete absence of oxygen or had had access to oxygen. Mirrors which had been exposed to the air were found to be resistant to concentrated nitric acid. On the other hand, mirrors which had been kept rigorously free from oxygen were immediately dissolved by concentrated nitric acid. As the latter observation appears to be contrary to what is generally understood to occur, it is necessary to point out that the iron mirrors deposited from iron pentacarbonyl vapour were exceedingly thin—so thin, in fact, as to be transparent. When thicker mirrors were used, they were attacked momentarily by concentrated nitric acid, the originally opaque deposit of iron becoming transparent, but the thin mirror of iron remaining was not further attacked.

The observations seem to suggest that when an air-passive film is already present on iron the main function of the concentrated nitric acid is to repair and strengthen this film. On the other hand, when the surface of the iron is completely free from oxide a certain amount of iron is dissolved before the protective oxide film is completely formed. An exceedingly thin film of iron may never show signs of passivity towards concentrated nitric acid. It was found in some experiments that after the dissolution of the iron mirror there remained portions of a thin, brown film, insoluble in nitric acid.

Evidence that the Passive Film is Ferric Oxide.

Although the isolation by Evans of a film of ferric oxide on iron rendered passive by air or by potassium chromate solution leaves no doubt that in these cases the chemical inertness of iron is due to a protective film, it appeared

impossible to isolate such a film on iron made passive by concentrated nitric acid, because of the spontaneous breakdown of the passivity after withdrawal of the metal from the nitric acid. When pieces of electrolytic iron were dipped below acid of d 1·4, then taken out and allowed to drain, after some seconds a violent reaction would start quite suddenly at some point and travel rapidly over the whole area.

E. S. Hedges (*J.C.S.*, 1928, 969) has conducted experiments, using methods that do not involve the removal of the metal from the acid, which indicate that iron rendered passive by nitric acid also has a protective oxide film and that this film consists of ferric oxide.

The first set of experiments aimed at obtaining evidence that passivity is a surface effect. If the passive metal is coated with an oxide film, it may be expected that this film will be washed or torn off when the metal is whirled rapidly in the liquid, so that the iron will become active and dissolve. On the other hand, according to the view advanced by Smits ("Theory of Allotropy," 1922, p. 345), the more rapid removal of ions from the metal by a high speed of rotation will produce a more violent disturbance of the inner equilibrium at the surface of the metal, and the iron will tend to become more passive.

In order to conduct these "whirling" experiments under the most sensitive conditions, it was first necessary to determine the minimum concentration of nitric acid which would suffice to passivate the iron. The experiments were conducted in a thermostat at 30° C., the solutions being made up by mixing measured quantities of nitric acid (d 1·42) and water from two burettes, so that the total volume of liquid (before admixture) was 10 c.c. For convenience, the mixtures are designated by the volumetric percentage of nitric acid used in their pre-

paration, a mixture prepared from 1·40 c.c. of water and 8·60 c.c. of nitric acid being referred to as 86 per cent. nitric acid.

The electrolytic iron used in these experiments was very kindly provided by Mr. U. R. Evans and was similar to that used by him in his experiments on the isolation of the protective film ; its manufacture and analysis are described on page 65. The material was pickled in dilute sulphuric acid, washed in water, dried, cut into pieces 1 cm. × 1 cm., and kept in a desiccator for twenty-four hours before use. By taking these precautions and ensuring that on entering the nitric acid the iron passed rapidly through the surface (see p. 119), reproducible values for the limiting concentration of nitric acid required to produce passivity were obtained.

The results of these preliminary determinations were as follows. Nitric acid of concentration 100 to 86 per cent. rendered iron passive, a distinct yellow colour being produced in 90 to 86 per cent. acid. When kept in these solutions, the passive iron dissolved so slowly that after three months very little dissolution had taken place. The lowest concentration of nitric acid required to passivate electrolytic iron at 30° C. was repeatedly determined as 86 per cent. In 85·5 per cent. acid the iron dissolved with great vigour and in 85·75 per cent. acid it dissolved quietly with the slow evolution of bubbles.

For the experiments on the activation of passive iron by whirling, pieces of iron foil 1 cm. × 2 cm. were pierced and suspended by a glass hook on the end of a glass rod, which could be rotated at a speed of 3000 r.p.m. in nitric acid. Iron whirled in nitric acid of any high concentration always imparted a distinct yellow colour to the solution after a short time, the more readily the greater the amount of water present. The following is typical of many experiments : The iron, resting

on the glass hook, was quickly passed through the liquid surface of 86 per cent. nitric acid and was observed to be passive ; it was then rotated at 3000 r.p.m., and no change occurred until after 30 seconds, whereupon the solution quite suddenly became deep yellow. After a further period of 60 seconds the iron had dissolved completely. Separate experiments showed that a similar piece of iron kept at rest in nitric acid of this concentration at 30° C. required eight days for complete dissolution.

These experiments show beyond doubt that passive iron becomes active when rapidly whirled in nitric acid. The " induction period " of about thirty seconds is of exceptional interest, for it seems probable that this represents the time taken to remove the protective oxide film, after which the dissolution proceeds apace.

Hedges has also made a study of the sudden transition of passive iron to the active state when heated in nitric acid. The experiments were carried out in a thin-walled test-tube containing 10 c.c. of the nitric acid solution and a piece of iron foil measuring 1 cm. × 1 cm. A thermometer was suspended in the nitric acid and the whole apparatus was immersed in a large beaker containing water, which was constantly stirred and heated by means of a small flame, so that the temperature was raised at the rate of 1° C. per minute. The iron was thrown quickly into the nitric acid at 30° C.

In the more concentrated solutions of nitric acid the following general sequence of events was observed on raising the temperature. At first the iron was passive and the solution almost colourless. At about 65° C. a faint yellow coloration appeared in the liquid, but suddenly at 75° C. slow evolution of small bubbles at the surface of the metal occurred ; this transition was quite sharp. The rate of evolution of gas

increased slowly thereafter until at a higher temperature dis-
solution of the metal occurred very suddenly with almost
explosive violence. In the following table are given the
temperatures of these two sudden changes of iron in solutions
of nitric acid of various concentrations :—

Conc. of acid, per cent.	.	100	99	98	95	90
1st temperature	.	74·5	74·5	75·5	74·5	75·0
2nd temperature	.	86·5	85·0	83·0	77·5	75·0

The table indicates that the first transition, corresponding
with the first evolution of gas, takes place at a definite tempera-
ture of 74·5° to 75·5° C. independently of the concentration
of the acid. The second transition temperature falls with
increasing amounts of water in the mixture, until, for 90 per
cent. nitric acid, the metal passes from the passive state directly
to the state of violent dissolution at 75° C.

The results may be interpreted as follows : The first
transition marks the change from passive to active metal, due
to dissolution of the film by the nitric acid ; the reaction is
slow, however, because the rate of dissolution of the film can
only just keep pace with its rate of re-formation as a result of
the reaction. The second transition, or violent dissolution,
denotes the complete disappearance of the film, and the tem-
perature at which it occurs falls with decreasing concentration
of nitric acid because of the greater solubility of ferric nitrate
in weaker nitric acid solutions.

In order to test this hypothesis, the effect of nitric acid on
ferric oxide was examined. Powdered ferric oxide was ignited
in a silica crucible, cooled in a desiccator, and immediately
placed in a test-tube containing 10 c.c. of nitric acid (*d.* 1·42).
At the ordinary temperature no coloration was produced in

the acid, and even when left for twenty-four hours at 30° C. only the faintest yellow was formed. The rate of dissolution of ferric oxide in nitric acid under these conditions is therefore very roughly comparable with that of passive iron. When the temperature was slowly raised, as in the experiments on the transition of passive iron, the first faint yellow colour was produced at 68° C. ; at 75°, the solution rapidly became deep yellow, and the thin deposits on the sides of the bottom of the tube vanished between 75° and 77°. The heating was continued up to 90° without further change other than a general deepening of the yellow colour. The total amount of ferric oxide dissolved was small. In an experiment carried out in 90 per cent. nitric acid, the first faint yellow colour appeared at 64° C., and the solution became deep yellow over the range 72° to 77°. It appears, therefore, that *the temperature at which passive iron in nitric acid becomes active coincides with that at which the rate of dissolution of ferric oxide becomes appreciable.*

Doubts have often been expressed concerning the existence of an oxide of iron capable of resisting the solvent action of concentrated acids, and statements are to be found in the literature of not many years ago to the effect that, apart from the inadequacy of known oxides of iron, it is necessary to assume that the oxide will be decomposed on heating to quite moderate temperatures in order to account for the activating effect. The experiments described show, however, that the latter assumption is absolutely unnecessary ; and the former objection is due to a misapprehension, for it is patent that freshly ignited ferric oxide dissolves in acids with extreme difficulty. Indeed, it is a point of great significance that the three metals which are most readily passivated (iron, chromium,

and aluminium) all give oxides which, when freshly ignited are hardly dissolved by acids.

Where chemical reactions or other processes are conditioned or inhibited by the formation of a film of one of the products, the course of the process (assuming the film to be continuous and impermeable) depends on the solubility of the film. The controlling factor in this case is not the *equilibrium solubility*, however, but the *rate of dissolution*. In the cases which have just been cited, possibly the velocity of dissolution of the oxides is controlled by the degree of hydration of the particles. For example, ordinary, powdered ferric oxide contains much adsorbed water and is much more readily soluble in acids than the ignited material. If this " loosely combined " water is present in relatively large amount, as in a ferric hydroxide gel, the dissolution by nitric acid is immediate. These considerations apply equally to the other oxides mentioned.

The reason for using freshly ignited ferric oxide in the experiments described above is that, since the protective film is formed under dehydrating conditions on immersing iron in concentrated nitric acid, the water content of the ferric oxide is bound to be low and its properties will approximate to those of the ignited material.

It is also noteworthy that passive iron does dissolve slowly in concentrated nitric acid, and it may reasonably be supposed that the rate is controlled by the rate of dissolution of the oxide. This view is in complete accord with all the phenomena observed on raising the temperature.

In addition to these experiments directly supporting the oxide-film theory of the passivity of metals, negative evidence was obtained which shows that the transition temperature does not mark anything in the nature of an allotropic change

in the metal itself.   Ordinary, active iron immediately becomes
blackened when placed in silver nitrate solution, through
deposition of metallic silver on its surface, whereas passive
iron remains unchanged.   If an allotropic change from passive
iron to active iron occurs at 75° C., then a piece of passive
iron, placed in silver nitrate solution, should cause deposition
of silver as soon as the temperature reaches 75°.   Actually,
it was found that iron made passive by nitric acid can be heated
in 0·2 N-silver nitrate solution to boiling without any deposi-
tion of silver occurring.   When the iron was kept for a long
time in the silver nitrate solution, glistening crystals of silver
were formed at isolated spots on its surface, evidently owing
to the presence of discontinuities in the oxide film.

Conditions which Render the Film Visible.

Periodic phenomena were observed in the experiments
on the activation of passive iron by raising the temperature.
In every case, at the transition temperature (75° C.) evolution
of gas started in puffs which were at regular intervals in any
one experiment, but the intervals varied from 1 to 9 seconds
in different experiments.   With rising temperature the fre-
quency of the periods increased.   In addition to the visible
changes in the state of the surface of the metal and in the
evolution of gas, these periods were accompanied by an audible
" pop," evidently caused by the suddenness of evolution of
gas at the commencement of each period.   Leaving aside for
the moment the intrinsic interest of these periodic phenomena
(which will be discussed in Chapter VI.), their existence offers
unusual opportunities of observing film formation.   The
growth of the film is repeated automatically at regular intervals
under the same conditions and, as the system is necessarily

in a sensitive state, the effect of slight modification of the conditions is easily observed.

In the periods observed in the activation of passive iron by raising the temperature the bright surface of the iron darkened during each rapid evolution of gas, the bubbles stopping when it became black ; as the surface brightened again, the evolution of gas slowly increased.   The cycle was repeated continuously.

In the conditions of these experiments the iron can only just become passive.   The film formed at this border-line state cannot be very protective ; it therefore grows to visible thickness.   At lower temperatures, where the conditions are not inimical to the permanence of a film, it is obvious that a film, once formed, will in virtue of its protective nature cease to grow.   In such a case the film will be exceedingly thin and invisible.   These observations on rendering visible the passive film on iron in concentrated nitric acid are in agreement with others, which show that a film will increase in thickness under the influence of an agency which can destroy it.

Shortly after these results were published a paper appeared by C. Benedicks and P. Sederholm (*Z. physikal. Chem.*, 1928, **138,** 123), describing the action of dilute (0·1 per cent.) alcoholic nitric acid on carbon steels.   It is maintained that the difference in the action of dilute and concentrated nitric acid on iron is due to the relatively slight dissociation of the concentrated acid, which therefore acts more as an oxidising agent than as a source of hydrogen ions.   Since the addition of alcohol represses the electrolytic dissociation of nitric acid, dilute solutions in alcohol may be supposed to have something in common with concentrated aqueous solutions.   These investigators showed that the dilute alcoholic solutions of nitric acid produce a passive layer on steel and succeeded in

photographing this film. They conclude that the film is a partly hydrated ferric oxide, but that on the inside of the film the iron atoms react with the ferric oxide to produce an inner layer of ferrous oxide, to which they appear to attribute the greater part of the protection afforded. If the formation of this inner, less highly oxidised film be admitted under these conditions, it must be remembered that a reducing agent, ethyl alcohol, was present and that the conditions are not those of violent oxidation comparable with the presence of concentrated nitric acid. There appears no reason to suppose that the passive film produced on iron by the action of concentrated nitric acid is other than ferric oxide.

The Periodic Passivity of Iron in Nitric Acid.

As will be shown in Chapter VI., periodic phenomena appear always to be accompanied by film formation. The periodic activity and passivity, observed by Hedges (see p. 103) on warming iron in concentrated nitric acid to the neighbourhood of the transition temperature, have been noted by others at the ordinary temperature in less concentrated solutions. About a century ago, J. F. W. Herschel (*Ann. Phys. Chim.*, 1833, **54,** 87) found that when iron was placed in nitric acid at a concentration just insufficient to render it permanently passive, the iron dissolved periodically, becoming alternately active and passive. In recent years this phenomenon has been made the subject of a more detailed examination by R. S. Lillie (*Science*, 1928, **67,** 593 ; 1929, 305 ; *Arch. di Sci. Biol.*, 1928, **12,** 103 ; *Proc. Soc. Exp. Biol. and Med.*, 1929, **26,** 317), who has shown in a particularly interesting way the great similarity between this periodic behaviour and the cardiac rhythm.

According to Lillie's experiments, periods are best obtained with pure iron in 70 per cent. (by volume) nitric acid, but they are not observed when iron is freely suspended in the acid. On the other hand, any local interference with diffusion, preventing free access of concentrated acid to a part of the metallic surface, favoured periodicity. For example, a regular rhythm was obtained when one end of an iron wire was inserted for a few millimetres inside a narrow glass tube, then immersing both in the acid. It appeared that the rhythm was always associated with a small local region in which the reaction between the wire and the acid was continuous, and from this region waves of activation travelled rapidly and periodically over the entire specimen. In the wire with one end in a glass tube, the enclosed portion undergoes continuous reaction with the acid, whilst the external portion is subjected to waves of activity and passivity, which are transmitted from the enclosed region. It is an interesting speculation that this region is similar to the nodal or " pace-making " region of the heart. The frequency of the periods can be varied by altering the length of wire enclosed in the tube. The frequency is dependent also on the concentration of acid, the temperature, electrical polarisation by an external current, and the composition of the metal. The kind of iron used determines the length of the non-transmissive or " refractory " period which follows a wave of activation. With pianoforte wire this may last several minutes, whilst in soft iron transmission may be possible again in less than a second.

The transmission of a wave of activation along a passive iron wire has unusual interest, since it is the nearest analogy we have to transmission along a nerve, and in both instances there follows a temporary, non-transmissive or refractory

period. Lillie considers that the properties of surface films are involved in both cases. In the passive iron system the spread of the wave of activation is marked by the breakdown and subsequent reinstation of the protective oxide film which is the cause of the passivity, and in biological systems surface films are also supposed to underlie the response of irritable tissues to irritation.

Passivity of other Metals at Low Temperatures.

Since the passivity of iron immersed in concentrated nitric acid is destroyed by heating to $75°$ C., it seemed possible that other metals, not showing passivity at the ordinary temperature, might become passive towards concentrated nitric acid at lower temperatures (Hedges, *J.C.S.*, 1928, 975).

Cobalt dissolved vigorously in nitric acid (*d.* 1·42) at the ordinary temperature, but became passive immediately at $-11°$ C. When the temperature was raised slowly the first bubbles of gas appeared at $+9°$, and at $25°$ a sudden vigorous dissolution set in. Thus, the phenomena are precisely similar to those observed with iron at higher temperatures.

Nickel is said to be rendered passive by nitric acid (*d* 1·42) at the ordinary temperature. Of six samples (not analysed) of nickel examined under these conditions, four were rendered passive and two were very rapidly dissolved. A specimen of the latter variety was immediately rendered passive when added to nitric acid at $-11°$ C. Again, the phenomena on warming resembled those observed with iron, for evolution of gas bubbles started suddenly at $30°$, and at $72°$ violent dissolution occurred.

Copper, when added to concentrated nitric acid at $-11°$ C., became covered with a visible, dark grey film and was inert,

very little dissolution taking place in two days at the ordinary temperature. On warming, sudden violent dissolution occurred at 40°. Thus, the complete analogy with iron is established. The passivity of copper produced by this method is not so durable as that of iron, for, if the copper be removed from the nitric acid, washed with water, and replaced, it is found to be active, dissolving with vigour. The reason is that the film of copper oxide is easily soluble in dilute nitric acid at the ordinary temperature, whilst ferric oxide is not. The fact that, in the case of copper, the oxide film has reached visible thickness is in itself an indication of its relatively poor protective value.

Zinc and *magnesium* were not rendered passive by nitric acid at $-11°$ C., but very slow evolution of gas occurred, suggesting that the metals were in the state between the two transition temperatures. On warming, dissolution set in at $-20°$ with such violence as to project the acid from the test-tube.

The Mechanism of the Reaction of Nitric Acid with Metals.

The discussion in Chapter II. on the kinetics of the dissolution of metals in acids with evolution of hydrogen shows that the reactions involved are more complex than the simple electronic exchange sometimes presented in text-books of electrochemistry. When nitric acid is the reagent, the numerous reduction products indicate even greater complexity of reaction, and the matter appears to have received little attention although it is of technical importance.

Previous investigators (J. J. Acworth and H. E. Armstrong, *J.C.S.*, 1877, **31,** 60 ; Freer and Higley, *Amer. Chem. J.*, 1899, **21,** 377) have studied primarily the gaseous products

of reduction of nitric acid at various concentrations by different metals (see summary by Bancroft, *J. Physical Chem.*, 1924, **28**, 474). Divers (*J.C.S.*, 1883, **43**, 465) classified metals into two groups in respect of their action on nitric acid : copper, mercury, silver, and bismuth produce water, nitrous acid, and the nitrate of the metal, whilst zinc, cadmium, magnesium, aluminium, lead, iron, and the alkali metals do not yield nitrous acid, but give ammonia and generally also hydroxylamine. It will be observed that one of these groups includes metals which do not disengage hydrogen from hydrochloric acid, and the other comprises metals which do so.

Two rival theories have existed for many years. According to one view, the first product of reaction of a metal such as copper with nitric acid is hydrogen, which does not appear as such, however, but, being in the nascent state, reduces the nitric acid to a variety of reduction products, depending on the conditions of reaction. It is urged in support that free hydrogen is obtained when magnesium acts on very dilute nitric acid. Supporters of the other view regard the metal itself as the reducing agent and deny the production of hydrogen.

Experiments conducted by E. S. Hedges (*J.C.S.*, 1930, 561) on the influence of rotation on the rate of reaction of some metals with nitric acid have shown that the metals fall definitely into two groups, the members of which are respectively electronegative and electropositive to hydrogen ; the hydrogen theory probably holds for the first group and the oxidation theory for the second.

The experiments were suggested by the accidental observation that some nitric acid in which an immersed copper sheet had been rotating for some hours had not acquired a blue colour. V. H. Veley (*J. Soc. Chem. Ind.*, 1889, **8**, 858 ; *Phil.*

Trans., 1891, **A.**, **182**, 279) had already observed that a rolling sphere of copper dissolved more slowly in nitric acid than a stationary sphere, and that the cause of the phenomenon was the removal of the nitrous acid, which acts as a catalyst, from the surface of the metal.

All the nitric acid used in the experiments described below was freed from nitrous acid by being warmed to $30°$ C. whilst a vigorous stream of air bubbles passed through it.   The metals were cleaned by etching with nitric acid.   The experiments were conducted in a thermostat at $30°$ and the loss of weight of the metal after immersion for one hour was determined.

The following table shows how the velocity of dissolution of copper in 25 per cent. nitric acid is greatly reduced by quite moderate rates of rotation ; a speed of 450 r.p.m. is sufficient to reduce the velocity of dissolution to a very low value :—

Speed (r.p.m.)	0	80	100	180	360	450
Loss of weight (grm.) .	1·312	0·259	0·131	0·079	0·014	0·003

The results indicate that the velocity of dissolution of copper in pure nitric acid is very low, and that some product of the reaction, which normally accumulates at the surface of the metal, is an active catalyst.   In the process of rotation, this catalyst is washed away from the surface as fast as it is formed, and consequently the reaction is slower than in the stationary state.   It should be possible, therefore, to increase greatly the velocity of dissolution of a rotating copper sheet by direct addition of the supposed catalytic reaction product to the nitric acid solution.   Copper nitrate, even in relatively large amounts (10 per cent.), did not increase the velocity of reaction, but the addition of small quantities of nitrous acid (in the form of sodium nitrite) was found to have an

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extraordinary accelerating influence, as is shown by the following results :—

| Sodium nitrite added, per cent. | . | 0 | 0·1 | 0·5 |
| Loss of wt. (grm.) | . . . | 0·003 | 0·171 | 0·622 |

Evidently, in agreement with Veley's conclusions, nitrous acid is the reaction product responsible for the high speed of reaction in the stationary state.

The next table gives similar results obtained for the dissolution of silver in 25 per cent. nitric acid :—

	Stationary.	At 450 r.p.m.	At 450 r.p.m. with 1 per cent. of $NaNO_2$.
Loss of wt. (grm.) .	1·174	0·000	1·187

Rotation of silver at 450 r.p.m. inhibited dissolution by nitric acid completely, and the solution gave no reaction for silver ions when tested with hydrochloric acid. The addition of 1 per cent. of sodium nitrite to the rotating system brought the velocity of dissolution to practically the same value as that of stationary silver.

On the other hand, the results obtained from similar experiments with tin in 25 per cent. nitric acid, zinc in 10 per cent. nitric acid, and magnesium in 5 per cent. nitric acid showed a striking difference from those for copper and silver. In these cases the rate of dissolution was *increased* by rotating the metal and nitrous acid had no accelerating effect.

The velocity of dissolution of copper in nitric acid is also reduced by adding to the nitric acid some urea, hydrogen peroxide, potassium permanganate, or other substance which can dispose of the nitrous acid as fast as it is formed. Actually, it was found that, in general, these reagents are less effective than rapid stirring in removing the nitrous acid. In the more concentrated solutions at 25° C. and in dilute solutions of

nitric acid at higher temperatures, nitrous acid is produced by the reducing action of copper at a rate greater than that at which urea or hydrogen peroxide can react with it.

This conclusion made it of interest to determine whether a considerably higher speed of rotation could prevent the dissolution of copper in nitric acid of density 1·42, and it was found that, although the reaction could not be stopped, its velocity was greatly reduced. For this purpose a piece of copper foil 1 cm. × 1 cm. × 0·01 cm., pierced and suspended by a glass hook, was lowered into an empty beaker and rotated at 2000 r.p.m. Concentrated nitric acid was then poured into the beaker. At rest, a piece of metal of these dimensions dissolved completely in the acid in less than 30 seconds, but when rotated at 2000 r.p.m., after an interval of about 6 minutes (during which the solution developed a green colour) the foil always left the hook, being still partly undissolved. The piece of copper left was observed to have a black skin and appeared to be passive, dissolving in the acid extremely slowly even when at rest. Some specimens were not completely dissolved after 60 minutes. An interesting behaviour was observed when one of these specimens was removed from the nitric acid and allowed to drain. After a few seconds, momentary effervescence appeared on the surface, the black film disappeared, and the metal was found to have lost its passivity towards nitric acid. This behaviour resembles exactly that of electrolytic iron which has been rendered passive by concentrated nitric acid, removed, and allowed to drain (see p. 100). It is probably caused by the tendency of the protective film to leave the metal-liquid interface and collect at the air-liquid interface.

These results suggest that, in the absence of nitrous acid,

nitric acid produces a protective oxide film on copper, which is thus rendered passive in a similar way to the better-known action of concentrated nitric acid on iron. The black film mentioned above resembled that observed on copper which had been rendered passive by immersion in concentrated nitric acid at $-11°$ C.

The metals which were examined in this investigation fall into two classes accordingly as the velocity of dissolution in nitric acid is increased or decreased by rotation. The presence of nitrous acid does not appreciably affect the rate of dissolution of members of the first group, but it accelerates very greatly that of metals of the second group. These groups are coincident with those of Divers (*loc. cit.*), who used as a basis of classification the nature of the reduction products. Members of the first group are electronegative to hydrogen and those of the second group are electropositive.
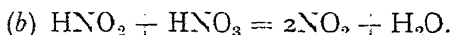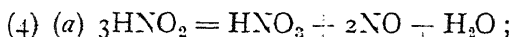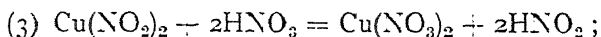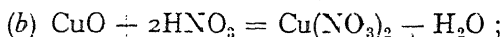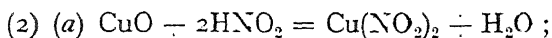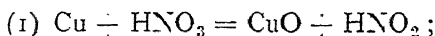
The electronegative metals can normally displace hydrogen from acids, and their behaviour provides no reason to doubt that they initially displace hydrogen from nitric acid; the hydrogen reduces the nitric acid to oxides of nitrogen and sometimes to ammonia and hydroxylamine. When the nitric acid is very dilute, hydrogen can be obtained in the free state by the dissolution of magnesium.

On the other hand, there is no *a priori* reason why the second group, consisting of electropositive metals, should displace hydrogen from nitric acid, since they do not do so from other acids.

The passivity phenomena observed when copper is rotated in concentrated nitric acid, observations on the anodic dissolution of copper in nitric acid, the observation of a difference of potential between stationary and rotating copper anodes in

nitric acid, and the formation of visible black films on the copper all suggest that an oxide film is formed on copper by the action of nitric acid.   There is also the fact that nitrous acid is produced and accelerates the reaction ; part of this acid reacts with the copper oxide, for, particularly in the early stages, the soluble product contains green copper nitrite as well as the blue copper nitrate, and part of it is decomposed to oxides of nitrogen, which are the gases evolved.

The suggested reactions may be represented thus :—

(1) $Cu + HNO_3 = CuO + HNO_2$;

(2) (a) $CuO + 2HNO_2 = Cu(NO_2)_2 + H_2O$;

(b) $CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O$;

(3) $Cu(NO_2)_2 + 2HNO_3 = Cu(NO_3)_2 + 2HNO_2$;

(4) (a) $3HNO_2 = HNO_3 + 2NO + H_2O$;

(b) $HNO_2 + HNO_3 = 2NO_2 + H_2O$.

In dilute acid 4 (a) gives nitric oxide as the main product, whilst in concentrated acid 4 (b) preponderates and the main gaseous product is nitrogen peroxide ; a mixture is usually produced.

If, by rotation or by the addition of a substance such as urea, the nitrous acid formed in (1) can be removed continuously, the metal becomes covered with a film of copper oxide and dissolves only slowly.   Nitrous acid may be said to " activate " the copper, perhaps in the same way that chlorine ions activate passive iron. The mechanism of this process of activation is not clear, but in some way the activating agent appears to loosen the protective film.

The theory outlined above supposes that cupric oxide can afford a sufficient degree of protection to the underlying metal, although ordinarily this substance is readily soluble in nitric acid.   To test this point, some rough experiments were carried

out on the rate of dissolution in nitric acid of samples of cupric oxide prepared in different ways. The method was to add 1 gram of the powdered oxide to 100 c.c. of 25 per cent. nitric acid, which was efficiently stirred at a constant rate by means of a glass stirrer, and to note the time taken for complete dissolution. It was found that cupric oxide prepared by ignition of the nitrate was relatively markedly resistant to dissolution. It is possible, therefore, for a form of cupric oxide to be sufficiently resistant to nitric acid to form a poorly protective film of the type required. The fact that the films are sufficiently thick to be easily visible is an indication of the low degree of protection afforded compared with that of the oxide film on passive iron. As fast as the relatively porous cupric oxide film is dissolved it is repaired by the nitric acid.

Thus, nitric acid appears to oxidise copper and silver superficially, causing them to become passive. Although in the dissolution of electro-negative metals in dilute nitric acid the displacement of hydrogen appears to be the first reaction, in concentrated acid the oxidation reaction may preponderate. Tin and iron form two excellent illustrations. Tin dissolves in dilute nitric acid, giving stannous nitrate, and the hydrogen reduces the nitric acid mainly to ammonia ; in concentrated nitric acid a hydrated stannic oxide is produced, but has not the requisite physical properties for forming a good protective coating. Similarly, iron dissolves readily in dilute nitric acid, but in concentrated nitric acid receives a thin film of ferric oxide which protects it from further action, and the iron is said to be passive.

Liquid-line Corrosion.

There are many instances of enhanced corrosion occurring at the liquid-line when a solid is partly immersed in a liquid

which has a chemical action on it, or which simply dissolves it. The phenomenon was first described by W. Spring (*Z. physikal. Chem.*, 1889, 4, 658) for calcite dissolving in hydrochloric acid and for sucrose and sodium carbonate dissolving in water. He concluded that the preferential dissolution was due to an enhanced reactivity of the solvent at the surface.

It is a familiar fact that when metals are partly immersed in corrosive liquids the degree of corrosion at the liquid-line is often greater than in the body of the solution.   In explanation, the protection of the immersed part by the downward flow of the reaction products and also the effect of atmospheric oxygen at the water-line have been urged.   Doubtless, many factors are involved and the reasons may be quite different in different cases, but some experiments by E. S. Hedges (*J.C.S.*, 1926, 831) appear to show that the phenomenon may still be observed in the absence of these causes, thus supporting the original view of Spring.

It must be admitted, however, that the effect of the liquid-line is very much more marked in the presence of substances capable of producing passivity than in a reaction such as the dissolution of zinc in hydrochloric acid ; it is particularly marked in solutions containing nitric acid. Half-immersed passive iron dissolves in nitric acid mainly at the liquid-line, and it seems that another aspect of the same phenomenon is the observation by Evans (p. 100) that the passivity of iron breaks down when the specimen is removed from nitric acid and allowed to drain, and the similar observation by Hedges (p. 115) with copper rendered passive by whirling in concentrated nitric acid. Evans (*J.C.S.*, 1927, 1020) considers that these phenomena are to be explained by the protective oxide film tending to leave the metal-liquid interface and collect at

the liquid-air interface, and this explanation seems to meet the particular case admirably.

Another surface difference was observed in Hedges' experiments (*J.C.S.*, 1928, 970) on the passivation of iron. It was found that in solutions of nitric acid containing 7 to 14 per cent. of water the production of passivity depends on the rate at which the iron passes through the *surface* of the liquid ; metal which was active as it passed through the surface became passive as it reached the bottom of the vessel. If one piece of iron foil was dropped gently with its flat side to the liquid surface and another piece was thrown edgeways through the surface, the first piece dissolved with great vigour, whilst the second piece was unattacked. This phenomenon is probably related to liquid-line corrosion. It is quite clear that the surface of nitric acid has less passivating influence than the body of liquid, and the tendency of the protective film to be loosened at such a surface is a tenable hypothesis.

The Activating Influence of Ions.

In the preceding pages it has been shown that the protective, passive film on iron in nitric acid is destroyed by rise of temperature and that it has a tendency to break down at the surface of the liquid. In addition, the film breaks down in the presence of certain electrolytes, the halides (particularly chlorides) being peculiarly active in this respect.

The pronounced peptising effect of chlorides on colloidal metal hydroxides has suggested that the cause of the activation lies in a loosening of the protective film thereby. On the other hand, it may be supposed that the action is electrolytic, chlorine ions being able to penetrate the oxide skin on the anodic

portions and thereby loosen it, whilst larger ions might not be able to penetrate the film.

U. R. Evans (*J.C.S.*, 1927, 1033) attempted to distinguish between these mechanisms by whirling discs of electrolytic iron in $M/20$-potassium chromate solution, washing, and then repeating the whirling in sodium chloride solutions under conditions which reduced differential aeration currents to a minimum. After this treatment the discs were still found to be passive, suggesting that mere immersion in a chloride solution is insufficient to activate passive iron and that anodic attack must be involved in the activation process. This view is supported by the fact that similar discs, after whirling in the chromate solution, were rapidly attacked when made the anode in $N/10$-sodium chloride solution, and also rusted when drops of $N/10$-sodium chloride were placed on the surface, the E.M.F. then being due to differential aeration.

The activating effect of ions on passive metals can be studied by measuring the potential of the metal in the solution against a standard reference electrode (calomel), a method of investigation which was employed almost simultaneously by A. L. McAulay and S. H. Bastow (*J.C.S.*, 1929, 85), by U. R. Evans (*ibid.*, 92), and by E. S. Hedges (*ibid.*, 1037). In the first two investigations mentioned, the potential-time curves of metals immersed in various solutions were constructed, whilst Hedges studied the variation of the potential of passive iron with the concentration of the activating agent. The potential of a metal covered with a discontinuous layer of another material lies between the potential of the metal and that of the coating material, but depends on the degree of discontinuity. Iron, covered with a discontinuous oxide film, will give a potential on the positive side of the potential of a clean iron surface ;

if the breakdown extends on immersion in a solution, the potential should move in a negative direction, whereas if the film becomes repaired it should move in a positive direction.

The results obtained by Evans with specimens immersed in $N/10$-potassium chloride solutions show that the breakdown of the protective film extends less quickly on iron treated with potassium chromate than on iron merely exposed to dry air for the same period, and also that the breakdown occurs more quickly on steel than on pure iron. Zinc showed a total change of only 0·04 volt, indicating that the oxide film on this metal has relatively little protective value—a conclusion which is in agreement with other work described in earlier chapters. Experiments with aluminium indicated that the film behaved in the reverse way, actually " healing " with time, the potential moving in the reverse direction.

The experiments of Hedges showed that, when iron is made passive in concentrated nitric acid, activation by hydrochloric acid occurs suddenly when a certain critical concentration is reached, a point to which further reference will be made in Chapter VI.

S. C. Britton and U. R. Evans (*J.C.S.*, 1930, 1773) have measured the penetrating power of different anions by determining the leakage current at an aluminium anode in a solution of potassium chromate, to which solutions of the ions under investigation were added. Normally, when aluminium is made the anode in potassium chromate solution a resistant oxide film is produced and very little current flows, but when a second salt is added a considerable current flows indefinitely, the strength of which depends on the nature and concentration of this salt. This current can be regarded as a measure of the penetrating power of the anion through the oxide film. For aluminium

the following decreasing sequence of penetrating power was obtained : chloride > bromide > iodide > fluoride > sulphate > nitrate > phosphate.   The anomalous position of the fluoride ion is worthy of note and is possibly due to its tendency to form larger complex ions, such as HF_2'.   It should also be pointed out that the nitrate ion, having oxidising properties, might tend to strengthen the film and thus suffer a reduction of penetrating power.   This aspect is well illustrated by experiments carried out on the same lines with a lead anode.   In this case, the decreasing sequence of penetrating power observed was : nitrate > chloride > bromide > iodide > phosphate > sulphate.   The solubility of lead nitrate and the insolubility of lead sulphate account for the changed order.

On the whole, the activating power of anions decreases with increasing size of the ion, suggesting that ease of penetration of the film is a controlling factor, but it may be suggested that in the same rough way a similar rule holds for peptisation. Here again the position of the fluorine ion is anomalous, its very low peptising effect being close to that of the bivalent sulphate ion.   It would be interesting to compare the activating effect of a series of electrolyte solutions on a passive metal with the peptising effect of the same solutions on the colloidal hydroxide of the metal.

A. W. Chapman (*J.C.S.*, 1930, 1546) has studied the influence of a soluble fluoride on the corrosion of iron and has found that whilst solutions of potassium fluoride of concentration less than $0.8\ N$ corrode iron in a manner similar to potassium chloride solutions of equivalent concentration, potassium fluoride solutions more concentrated than $0.85\ N$ do not corrode iron and have an inhibitive influence on the corrosive action of chloride ions.   This may be due to the formation of a

protective film of fluoride at the surface of the metal, but it is interesting to note also that the attack of a dilute fluoride solution was inhibited by potassium chromate in concentrations much lower than were needed for a chloride, again showing the comparative feebleness of the fluoride ion in loosening or penetrating the film.

Some interesting work on the activation of passive chromium has been carried out by E. Müller and K. Schwabe (*Z. Elektrochem.*, 1931, **37**, 185). Experiments on the activation of chromium by cathodic polarisation showed that a definite activation potential is required in different acid solutions. The negative potential at which activation occurs in normal acid solutions increases in the order : hydrochloric, hydrofluoric, hydrobromic, sulphuric, perchloric, orthophosphoric ; thus, activation is more easily brought about by small than by large anions. The experiments lead to the view that chromium in the passive state is covered by a network of chromic oxide molecules, which are anchored to the units of the chromium space-lattice. Acids cannot dissolve the oxide film except by penetrating between the molecules, and the size of the anion is all-important, therefore. As the cathodic polarisation is increased the small hydrogen ion is dragged through the oxide network, and the electrostatically-bound anion can follow it and dissolve the film, provided that the anion is not too large. At the corners and edges of the metal the oxide network is looser and anions can readily penetrate at such points, which therefore become active. A short-circuited cell is then set up, and if the potential reaches a higher negative value than the activation potential for the particular acid the whole metal will become active and dissolve. In the case of chromium at 20° C. this state is realised in hydrochloric acid only.

Periodic Phenomena in Activation.

In Chapter VI. are discussed many examples of electrolytic reactions in which, under the simultaneous influence of passivating and activating conditions, alternation between the passive and active states occurs periodically. Periodic activity and passivity can be realised in the absence of externally applied current. Whether the periodic dissolution of metals described in Chapter II. comes into this category is doubtful, but an observation of E. S. Hedges and J. E. Myers (*J.C.S.*, 1925, **127,** 1023) of some years ago has a new interest in this connexion when viewed in the light of subsequent work.

Copper sheet, after reduction by cold-rolling, was found to dissolve periodically in an acid mixture containing 25 c.c. of nitric acid (*d* 1·42), 10 c.c. of hydrochloric acid (*d* 1·16), and 65 c.c. of water ; gas was evolved at regular intervals of about three minutes and the potential of the metal, as measured by an electrometer, underwent a synchronous periodic variation. Annealed copper did not show this phenomenon, the reason for the difference not being clear.

The series of changes to be observed at the surface of the dissolving metal under these conditions is most striking. Initially, the surface preserves its natural colour : then there is a sudden appearance of a black film deposited in the form of vertical streaks : the black film next turns dull grey : this is followed by a sudden flash, due to the film turning white : the film then dissolves, leaving the metal with its original colour. Then the black film forms again, the whole cycle being repeated in each oscillation.

The onset of the black film is marked by a movement of the electro-potential in the positive direction and by an increase in the rate of evolution of gas, whilst, corresponding

with the gradual turning grey of the film, the electro-potential and the gas pressure slowly move towards their former values. The sudden appearance of the white film is accompanied by a rapid change of the electro-potential in the negative direction and an equally rapid increase in the rate of production of gas. The latter effect is easily visible, resembling a miniature eruption. As the white film dissolves, both the electro-potential and the gas pressure regain their initial values.

There is scarcely any doubt that the black film is cupric oxide and that the white film is cuprous chloride.   The phenomena are reminiscent of those observed in activating passive iron in nitric acid by raising the temperature (p. 103), and the black film recalls that observed on copper in nitric acid under other conditions.   Nitric acid oxidises the copper superficially, in accordance with the scheme given on p. 117, but whilst the oxide film is normally invisible, the presence of the activating hydrochloric acid, which can destroy it, causes it to grow to visible thickness.   The hydrochloric acid eventually transforms the cupric oxide, having a copper backing, to cuprous chloride, which then dissolves in the acid solution.   In the light of data presented in Chapter VI., the cause of the periodicity must be ascribed to the fact that a critical concentration of hydrochloric acid must be reached in order to break down the film of cupric oxide.

This peculiar behaviour of copper in a mixture of nitric and hydrochloric acids was subsequently made the basis of an alternating-current cell by Hedges (*J.C.S.*, 1926, 1892). A small plate of rolled copper and another of annealed copper were immersed in a solution consisting of 25 c.c. of nitric acid (*d* 1·42), 10 c.c. of hydrochloric acid (*d* 1·16), and 70 c.c. of water. This combination gave a unidirectional periodic

current varying between 30 milliamperes and zero. An alternating current may be produced by using two electrodes of cold-rolled copper in the solution specified. As a rule, the positive and negative currents are asymmetrical, for the probability is that the electrodes will be neither quite in phase nor quite out of phase. The maximum difference of E.M.F. obtainable from this cell is 0·14 volt and the frequency is about one cycle per minute.

CHAPTER VI.

ANODIC FILMS.

IN the early part of the nineteenth century, those who experimented on the passivity of iron in concentrated nitric acid were aware that this peculiar state was more readily brought about when the iron was in contact with a more electro-positive substance, such as platinum, and that activation was effected by contact with an electro-negative metal, such as zinc. It is also clear from Faraday's writings that the passage of electricity was involved in these phenomena and had some connexion with passivity. That is to say, when iron is in contact with platinum the iron becomes anodic and is more readily rendered passive than when electrically neutral. Later investigators began to study passivity by applying the anodic treatment by means of an external battery rather than by contact with an electro-positive metal.

When a metal is made the anode of an electrolytic cell it may exhibit more than one type of behaviour. (1) It may be unattacked by the liberated anions and lead to the evolution of oxygen (*e.g.* platinum); (2) a film of insoluble and poorly conducting material, practically preventing further passage of current, may form on the metal (*e.g.* silver in a chloride solution); (3) the metal may dissolve continuously to form a salt (*e.g.* copper in dilute sulphuric acid at low current densities); or (4) the metal may dissolve smoothly at low current densities,

whilst with increase of current a film may form. When process (4) occurs the current passing falls and the potential of the anode rises on formation of the film ; dissolution of the metal may continue at a slower rate, giving perhaps ions of higher valency (cobalt gives a cobaltic salt in sulphuric acid of certain concentrations, whilst chromium gives chromic acid), or the metal may become passive, scarcely dissolving at all, whilst oxygen is freely evolved (e.g. iron in dilute sulphuric acid).

It will be apparent already that there is some confusion concerning what is understood by anodic passivity, some authors meaning thereby that the metal dissolves at an abnormally high potential, whilst others use the term to indicate that the metal scarcely dissolves at all. The work described in this chapter shows that these different aspects are very closely connected.

It is clear, also, that in electro-refining and in electro-plating passivity is a technically important evil, since it leads to waste of power, interferes with the control of the optimal current density, and may cause the bath to become impoverished of salts. A proper understanding of anodic phenomena is essential, therefore, in these industries, but in the past little attempt has been made to undertake a systematic study of the subject. During the past few years systematic researches have been carried out by W. J. Müller and his school in Vienna, and by E. S. Hedges in London, and it is proposed to discuss this work in some detail. It is gratifying that whilst these investigations have been carried out concurrently from different aspects and although the authors have placed different interpretations on certain aspects of the results, in the main there is considerable concordance of results and agreement concerning the principal features of anodic polarisation.

9

The Work of W. J. Müller.

The brief summary given below is taken from the following papers : Müller, *Z. Elektrochem.*, 1924, **30,** 406, 696 ; *ibid.*, 1927, **33,** 403 ; 1928, **34,** 571 ; 1929, **35,** 656 ; *Monats.*, 1927, **48,** 61 ; Müller and E. Noack, *ibid.*, 1927, **48,** 293 ; Müller, *ibid.*, 1927, **48,** 559 ; Müller and K. Konopicky, *ibid.*, 1927, **48,** 711 ; Müller and O. Löwy, *ibid.*, 1928, **49,** 47 ; Müller and Konopicky, *ibid.*, 1928, **50,** 861 ; Müller and Löwy, *ibid.*, 1929, **51,** 1025 ; Müller, *ibid.*, 1929, **52,** 221 ; Müller and Konopicky, *ibid.*, 1929, **52,** 289 ; Müller and L. Holleck, *ibid.*, 1929, **52,** 409, 425 ; Müller and Konopicky, *ibid.*, 1929, **52,** 442, 463 ; Müller and W. Machu, *ibid.*, 1929, **52,** 474 ; Müller and Konopicky, *Z. physikal. Chem.*, 1929, **141,** 343 ; 1929, **145,** 241.

The characteristic experimental arrangement in Müller's work is the anode, consisting of a metal cylinder, the flat top of which is in contact with the solution, whilst the other sides are protected from the solution by glass. The anode surface is thus in a horizontal position and hence the products of reaction remain where they are formed ; when vertical anodes are used the reaction products stream downwards from the electrode and cause currents to be set in motion ; these convection currents are very important in determining the conditions for passivity. In the experimental arrangement described, the surface of the anode is further protected from disturbances in the main body of the solution by means of a glass hood.

Making a study of the current density-potential curves for anodes of different metals in various solutions, reproducible values could be obtained with this apparatus for the current density at which the potential rose suddenly to a higher value, indicating passivity. But the important feature brought out

by these curves is that the time during which the current must
flow before the sudden change to the passive condition sets in
depends on the current density ; that is to say, passivity can
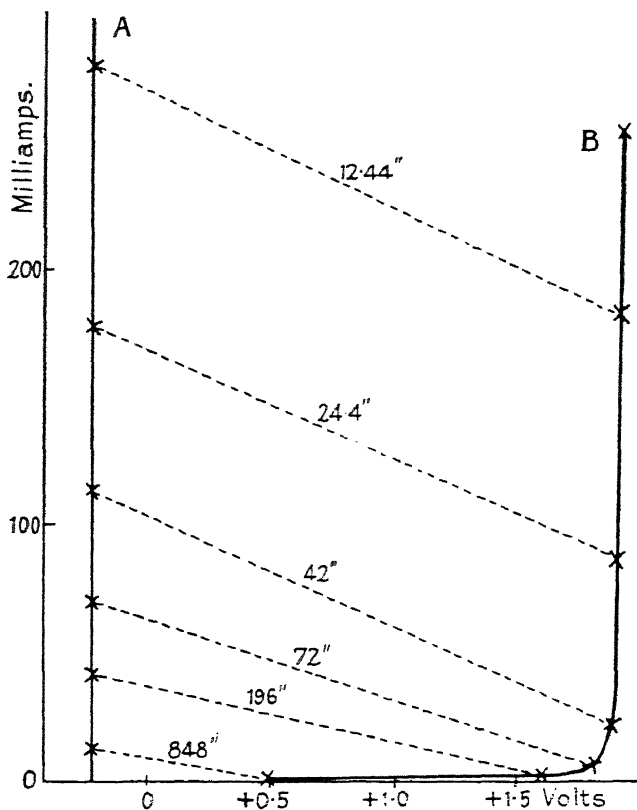be brought about by a small current acting for a long time or

FIG. 14.—The time-effect in anodic passivity.

by a large current acting for a short time. Fig. 14 has been
reproduced from some of Müller's results for an iron anode
in dilute sulphuric acid. Curve A shows the relation between
current density and potential for the active electrode, dissolving
as ferrous sulphate, and curve B connects the points reached

when the metal becomes passive. In each case the time required for the transition to the passive state is indicated, and it will be observed that the time decreases as the current density increases.

This relation between current density and time of passivation suggests that some substance must accumulate at the anode before passivity can set in : a conclusion which has been developed independently by Hedges from quite a different point of view. The view expressed by Müller is that some product must accumulate until the solution becomes supersaturated in the immediate vicinity of the electrode, whereupon a solid crystallises out on its surface. This deposit covers a large part of the surface of the anode and increases the effective current density at the uncovered portions, perhaps to 100 or 1000 times the original value. This high increase in current density causes the anode potential to rise to a value at which the reactions characteristic of the passive state are possible. Whilst Hedges has developed the view that this change consists in the formation of a protective oxide film at the surface of the anode, Müller believes that the high potential brings about some change in the electronic state of the metal in the surface layers, so that it either ceases to dissolve or begins to dissolve as ions of a higher valency.

It is not suggested that the visible film of reaction product which forms on the anode is responsible for passivity, but that by screening a large part of the anode it leads to conditions which cause passivity. Müller calls the first stage " Bedeckungspassivität " and the second stage " chemische Passivität."

By measuring the rate of fall of current with time an idea has been gained of the composition of the first reaction product which accumulates on the anode, and this has been con-

firmed by direct observations with a polarising microscope, which has enabled actual photographs of the film causing " Bedeckungspassivität " to be taken. The composition of the initial deposit appears to vary in different cases. With sulphuric acid solutions as the electrolyte, the first deposit on an iron anode is probably hydrated ferrous sulphate. In the following table the times of passivation of an iron anode in sulphuric acid solutions of different concentrations at constant current density are compared with the solubility of hydrated ferrous sulphate in the same solutions:—

Concentration of Acid (N).	Time of Passivation (sec.).	Solubility of $FeSO_4, 7H_2O$.
0·06	0·22	—
0·24	0·26	—
0·48	0·60	—
0·94	1·84	1·36
1·75	2·99	1·28
3·13	2·99	1·16
4·88	2·1	1·02
9·14	1·54	0·73
13·2	0·92	0·43

The table shows that at concentrations greater than about $3N$ the time of passivation decreases with increasing concentration of the acid and corresponds with the decreasing solubility of ferrous sulphate. Evidently, the decrease of time of passivation with decrease of concentration below $1·75N$ cannot be ascribed to the same cause, and in these dilute solutions Müller supposes that the covering layer consists of basic salts. This supposition is in agreement with the conclusions of Hedges (p. 142) reached by experiments in dilute sulphuric acid solutions. In the case of a copper anode in sulphuric acid solutions the time of passivation is parallel to the solubility of copper sulphate pentahydrate throughout ; with zinc the first anodic

product was recognised by polariscopic observation as zinc sulphate heptahydrate, changing to a basic salt; the deposit on chromium is usually a basic chromium salt or even chromic hydroxide.

Müller has further investigated the relations between the growth of the deposit and the fall of current with time. Assuming that the thickness of the deposited layer remains constant and that the film grows sideways only, the fall of the current i with time t is given by the expression

$$t = C + A\left[\frac{i}{i_0 - i} + \frac{2 \cdot 3}{i_0} \log \frac{i_0 - i}{i - i_R}\right],$$

where i_0 is the initial current, i_R is the residual current which leaks through, C and A are constants defined by the formulæ

$$C = \frac{s \eth F}{k(1 - u)i_0} \quad \text{and} \quad A = \frac{s \eth^2}{Kk(1 - u)w_0},$$

where s is the specific gravity of the material of which the layer is composed, $\eth$ its thickness, F the original area of the anode surface, k the electrochemical constant, u the anionic transport number, w_0 the resistance from the cathode to the boundary layer adjacent to the anode, and K the conductivity of the solution in the boundary layer.

This sideways-growth relation has been found to hold in sulphuric acid as the electrolyte for anodes of copper and also for anodes of iron or nickel in the early stages. In the later stages anodes of iron or nickel follow a course which can be related to growth in thickness, without sideways extension. In this case the currents i_1 and i_2, passing at the times t_1 and t_2, are connected by the relation

$$t_2 - t_1 = B\left(\frac{1}{i_1^2} - \frac{1}{i_2^2}\right),$$

where B is a constant depending on the area uncovered. This relation of growth in thickness also holds for anodes of zinc, aluminium, and lead.

The experiments on the anodic behaviour of aluminium in sulphuric acid solutions have thrown an interesting light on valve action. The unidirectional passage of current through such a system has been supposed by A. Günther-Schulze and others to be due to a layer of oxygen gas at the surface of the anode. Müller and Konopicky have analysed this gas and found it to be mainly hydrogen. As the time-relations of the aluminium anode are in accordance with the equation denoting growth in thickness, they relate the phenomenon to the growth of a solid film on the surface of the anode, and explain the unidirectional nature of the conductivity by supposing that the aluminium anode becomes covered with a gelatinous layer of colloidal aluminium hydroxide. During each anodic period the gel, which is negatively charged, is pressed tightly against the anode by cataphoresis, the liquid is squeezed out and no current can pass. During each cathodic period the negative gel moves away from the electrode, liquid enters and the insulation thus breaks down.

In his later work (see especially *Trans. Faraday Soc.*, 1931, **27,** 737) Müller definitely accepts the existence of a protective oxide film at passive electrodes, but still holds to the view that its formation is preceded by an electronic change in the metal in the case of those metals which can exist in more than one state of valency. Applied to the case of an iron anode, it is supposed that after formation of the primary layer the high-current density at the uncovered portions of the electrode produces a change in the metal there which induces it to go into solution as ferric ions. The ferric salt thus formed

hydrolyses and produces on the anode a protective oxide film at which oxygen is then evolved. Müller regards this as true chemical passivity, whilst in the case of an aluminium anode where no change of valency can occur, he regards the whole process as " Bedeckungspassivität," the film having a highly protective value.

In its new form, Müller's theory agrees even more closely with that developed in the subsequent pages. Whether the change of valency which is observed in some cases is a primary or secondary change, there is now almost universal agreement that anodic passivity, like other forms of passivity, is characterised by the possession of a protective film.

The Study of Periodic Film Formation at Anodes.

Contemporaneously with the researches which have just been described, E. S. Hedges has carried out a series of investigations on the formation of anodic films, particularly under conditions such that the film automatically appears and disappears periodically. Apart from the intrinsic interest of periodic physico-chemical phenomena, as the process under observation is repeated automatically at regular intervals of time, these conditions are peculiarly favourable for the study of film formation.

The experimental method was to electrolyse various solutions with an anode of the metal being studied and a cathode of platinum foil. The anode was a rectangular sheet of pure metal and was suspended vertically in the solution. Current density-potential curves were constructed for the different systems and were compared with the visible changes occurring at the surface of the anode. In the early experiments the potential drop across the two electrodes was measured by means

of a voltmeter of suitably high resistance placed across the terminals, but in the later work the anode potential was measured against a standard normal calomel electrode by means of a string electrometer. The experiments described were conducted in a thermostat at 30° C., except where stated otherwise.

Copper Anodes.

Experiments in which a copper anode was used (Hedges, *J.C.S.*, 1926, 1533) showed that when fairly concentrated hydrochloric acid is electrolysed at low-current densities the copper passes into solution at the anode as cuprous chloride. As a rule this may be seen as a white coating on the metal, but does not appreciably impede the course of electrolysis. In the absence of atmospheric oxygen no cupric salt is formed. At high-current densities a film which appears to be cuprous oxide forms over the metal ; this film is highly resistant and the current passing falls to a low value ; the electrode still continues to dissolve slowly, but a small portion of the residual current is employed in the liberation of oxygen, a few bubbles of which rise from the anode. At intermediate current densities the two effects alternate, the seat of the phenomenon being the anode, at which visible periodic changes occur.

The current density-potential curve of this system is represented by Graph 58 in Fig. 15, which shows the effect of gradual increase of current density in the electrolysis of hydrochloric acid, containing 25 c.c. of acid (*d* 1·16) in 100 c.c. using a copper anode and a platinum cathode. For values below 60 milliamps. per cm.² the potential rises slowly along the line AB ; cuprous chloride is formed at the anode and dissolves in the hydrochloric acid, and at the cathode copper is

deposited and hydrogen evolved.   At the value corresponding
to the point B the potential oscillates in regular periods between
0·55 and 10·6 volts, and simultaneously the current fluctuates
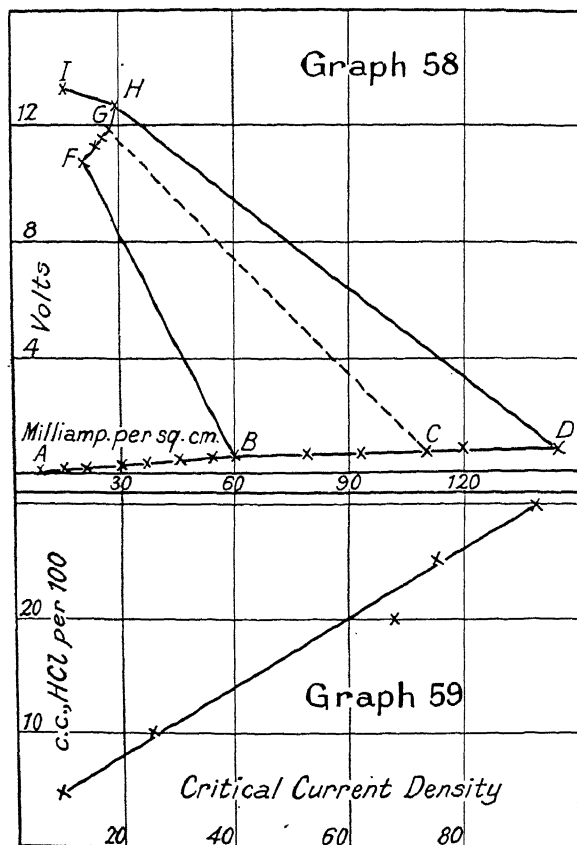between 60 and 20 milliamps. per cm.[2].   The region of regular

FIG. 15.—Current density-potential curve for copper in hydrochloric acid.

oscillations continues as the current density is increased along
BD to the value 145 milliamps. per cm.[2], the amplitude here
being from 1·0 to 12·7 volts.   At an intermediate point C
the values of current density and potential oscillate between

points C and G. At current densities greater than 145 milliamps. per cm.² the potential immediately rises (the current falling) to a value corresponding to the point H, at which it remains constant, periods being no longer observed. Further attempts to increase the current are unsuccessful, for the anodic film becomes more and more resistant and the effect is actually to decrease the current still further, along the line HI. The electrode exists in one state, therefore, along AB, in another state along HI, and the area BFHD marks a region of instability, where the electrode oscillates regularly between the two states.

The point B represents the critical current density required to produce the oxide film, which forms periodically under these conditions, and its value increases with the concentration of the hydrochloric acid and with rising temperature. The critical current densities required to produce the film in a series of solutions containing from 5 to 30 c.c. of hydrochloric acid in 100 c.c. of solution have been determined and are plotted in Graph 59 (Fig. 15), which indicates a direct proportionality between critical current density and concentration.

The frequency of the periods varies with the conditions, decreasing with increasing current density, and increasing with rise of temperature, with increase of concentration of the hydrochloric acid and with vigorous stirring. In general, under the conditions described the order is about one cycle per minute.

The visible features of film formation in this system are particularly well marked and correspond with the periodic changes in potential and current density. Simultaneously with the sudden rise in the potential there sweeps *up* the metal a very thin, dark grey film. After a short interval, the current begins to increase, slowly at first and then suddenly, while the potential rapidly resumes its initial low value and a white

film sweeps *down* the anode. The series of changes is repeated in each successive wave. The first film has the appearance of cupric oxide rather than cuprous, but there is doubt in assigning a composition to so thin a film. It is believed to be cuprous oxide, for it gives cuprous chloride with hydrochloric acid and no cupric salt is produced in the reaction. There is no doubt that the white film is cuprous chloride.

It has been observed that wherever deposition of a film occurs in electrolysis, this starts at the sides and lower part of a vertical, rectangular electrode and travels up the electrode in the form of a U of diminishing concavity. This seems to be due to the concentration of current density at the corners and edges of the electrode and accounts for the manner in which the dark oxide film travels up the anode. The downward sweep of the cuprous chloride film has been traced to the flow of hydrochloric acid down the electrode, due to the sinking of the reaction products which is observed even when the solution is mildly stirred. By allowing a stream of air or hydrogen bubbles to impinge on a point near the bottom of the anode, the reaction product can be washed upwards, and under these conditions the cuprous chloride film travels upwards also ; but the oxide film could not be made to travel downwards. The phenomenon may be localised by directing a stream of air bubbles on a point about half-way up the electrode, when the small area of metal affected by the rapid stirring exhibits rapid black and white flashes, while the main part of the electrode performs its slow periods unhindered. The record of potential then consists of short waves superimposed on the long waves ; a point of some interest relating to the complicated periods sometimes observed in the dissolution of metals in acids (*cf.* Chapter II.).

Somewhat similar phenomena were observed with copper anodes in potassium cyanide solutions. In 2·5 and 5 per cent. solutions of potassium cyanide anodes of copper rapidly become enveloped in a golden-green film, generally described as a basic cyanide, which readily dissolves in the electrolyte when the circuit is broken. The phenomena are more definite in a 10 per cent. solution ; at low-current densities no film forms over the anode and the copper dissolves as potassium cuprocyanide. When the current density is raised to 59 milliamps. per cm.² a dark grey oxide film sweeps up the metal, and the potential difference across the electrodes rises from 1·6 to 2·7 volts. After a few seconds the dark film gives rise to a white film, presumably of cuprous cyanide, which travels down the metal, and the potential resumes its former value. The two states oscillate thereafter in regular periods.

The limits of the conditions favouring periodicity in the cyanide solutions are, however, very much narrower than in the chloride solutions. If a current density-potential curve similar to Fig. 15 be constructed for the cyanide solution the region of instability BFHD is very short and is indeed easily overshot, the electrode often going straight from the state represented by B to that represented by H. It is only by increasing the current density cautiously that the intermediate oscillating condition can be realised in this system.

When the current density is further increased to 86 milliamps. per cm.² a pale green film permanently covers the anode. At this stage cuprous cyanide is being formed more quickly than it can dissolve in the potassium cyanide solution. The onset of this film is marked by a rise of potential from 3·6 to 6·2 volts, after which a second series of oscillations ensues. The frequency of these periods varies from 0·1 to 5·0 seconds.

Experiments with a copper anode in sulphuric acid solutions of various concentrations revealed that in solutions containing more than 50 per cent. (by volume of acid, d 1·84) very little current would pass, the potential rapidly rising to a high value. After a time cupric sulphate could be seen as crystals on the anode. In solutions containing less than 10 per cent. of sulphuric acid the copper dissolved steadily and without marked change of potential at all the values of current density employed, although loosely adherent cupric oxide was formed, but at intermediate concentrations the potential rose to a high value at a certain critical current density. In no case was a periodic effect produced and the conclusion was reached that the highly resistant film in this case is copper sulphate ; a view which was confirmed a little later by Müller's more detailed work on this system.

In solutions of nitric acid containing less than 10 per cent. (by volume), electrolysis with a copper anode pursued a steady course over the whole range of current densities, but at the end of each experiment the anode was found to be covered with a slimy, black deposit, probably of cupric oxide, which did not increase the resistance of the system. Some more detailed experiments on the anodic dissolution of copper in 25 per cent. nitric acid were carried out later (Hedges, *J.C.S.*, 1930, 566), measuring the loss of weight of the anode during a given time interval. The following table shows the loss of weight of the anode both when stationary and when rotated at 400 r.p.m. for one hour at various current densities. The last column gives the loss of weight to be expected in accordance with Faraday's law :—

Current Milliamps.	Loss of Weight Grams .		
	Stationary.	At 400 r.p.m.	Calculated.
0	1·312	0·01	0·000
25	1·158	0·096	0·592
50	0·790	0·270	1·185
100	1·000	0·280	2·369
500	1·314	0·586	11·848

It will be observed that in every case the rotating anode dissolves more slowly than the stationary anode, although at the higher current densities the difference is relatively less. At 25 milliamps. the loss is about twice as great as that calculated from Faraday's law, which means that much of the dissolution is controlled by local short-circuited electrolytic cells in the metal, the electrical energy of which is not registered on the external circuit. At higher current densities the loss is much less than is required by this law, the discrepancy increasing with the intensity of the current. In these cases evolution of gas at the cathode was observed, so that only a portion of the electrical energy is involved in the formation of cupric ions. Thus it appears that copper readily becomes passive, though incompletely so, under anodic polarisation, and the more readily so when the copper is rotated, *i.e.* in the absence of nitrous acid. At the end of these experiments the electrodes were observed to have a black or grey film over the surface. In performing the experiments the anode and cathode compartments were separated by means of a porous pot.

In dilute solutions of sodium hydroxide oxygen was readily evolved at a copper anode. In 8 per cent. sodium hydroxide solution at current densities below 5 milliamps. per cm.^{2}

a resistant film of cupric oxide slowly formed on the anode, the potential difference increasing from 1·2 to 2·3 volts, at which oxygen was evolved. The visible film disappeared at higher current densities and a greenish-yellow substance could be observed going into solution. Periods were not observed in these systems. In 5 per cent. and 1 per cent. solutions of potassium iodide or chromate insoluble films immediately formed over the anode.

Silver Anodes.

In 5 per cent. potassium cyanide solution a silver anode dissolves normally as potassium argentocyanide when the applied potential is less than 2·3 volts ; at this value a brownish-black film of cupric oxide sweeps up the metal and the potential rises to 3·2 volts and then oscillates rapidly (about twice per second) between 3·2 and 3·0 volts. Simultaneously, the upper part of the anode displays alternate black and white flashes— a rapid periodic dissolution of the silver oxide film by the potassium cyanide. The phenomenon is precisely similar to that shown by copper, the black oxide film sweeping up and the white cyanide film rolling down, the frequency increasing with current density, concentration, and temperature. On slightly increasing the current, the alternation is so quick as to resemble a twinkling. Similar effects were observed in more dilute solutions. A 2·5 per cent. solution gave periods having an amplitude of 0·4 volt between the critical limits 1·7 and 2·9 volts ; below the value 1·7 no oxide film appeared, and above 2·9 it existed permanently. The extent of the unstable region decreases with progressive dilution, for the limiting voltages for a 1 per cent. solution were 1·8 and 2·7, for a 0·5 per cent. solution they were 1·8 and 2·4 and for a 0·25 per cent. solution 1·6 and 1·7 volts.

When solutions of ammonium chloride were electrolysed with a silver anode, a highly resistant film of silver chloride was formed immediately. Attempts were made, therefore, to add just sufficient ammonia to dissolve the film as fast as it formed. Periodic effects were observed in these experiments, the anode becoming intermittently coated with a dark brown oxide film. The best result was with a solution of 50 c.c. of 10 per cent. ammonium chloride and 50 c.c. of ammonia solution (d 0·880). With a current density of 44 milliamps. per cm.² the potential difference oscillated between 3·0 and 4·1 in periods of 20 seconds.

In sulphuric acid a silver anode dissolved continuously only in the most concentrated solutions, a sulphate film forming above a certain critical current density and the potential rising very sluggishly. Periods were obtained in these systems at higher temperatures. The solution always became cloudy with silver sulphate, preventing observation of the state of the anode.

Zinc Anodes.

At low current densities a zinc anode dissolves in sodium hydroxide solution with formation of sodium zincate. At higher current densities a film forms over the metal, the potential rises, and oxygen is evolved, but at the same time the zinc continues to dissolve. By suitably reducing the current a region of oscillating potential is encountered.

The current density-potential curve (Hedges, *J.C.S.*, 1926, 2581) is represented by Graph 50 in Fig. 16, which refers to 8 per cent. sodium hydroxide solution. For low values of current density the potential rises along the line AB until the critical value 72 milliamps. per cm.² is reached. At this point

a film forms over the electrode and the potential difference rises from 1·1 to 3·1 volts (C). After the lapse of a second or so, evolution of oxygen ensues and the potential difference rises to 3·9 volts (C'). Further increase of current density causes the potential difference to rise slowly along the line
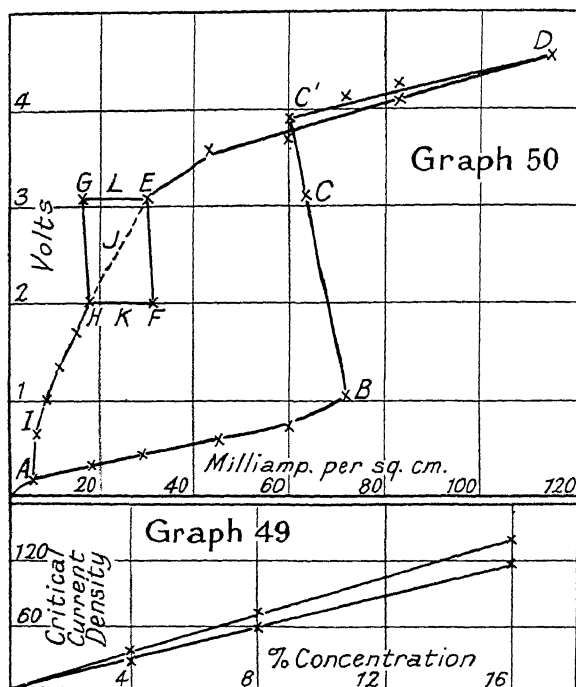

FIG. 16.—Current density-potential curve for zinc in sodium hydroxide solution.

C'D. If the current is now gradually reduced, the potential retraces approximately the same path and continues to the point E. If an attempt is made further to reduce the potential along EJH, it falls of its own accord to a considerably lower value and then regains the value 3·0 volts by a series of *damped* oscillations, *i.e.* the potential oscillates with damping between

the values represented by E and F, L and K, G and H, etc. The point H represents the lower limiting current density for periodicity, and on further reduction the potential falls along HI and at the point I decreases rapidly.

Examples of the damped oscillations are given in Graph 46 (Fig. 17), where A shows the rapid damping when the
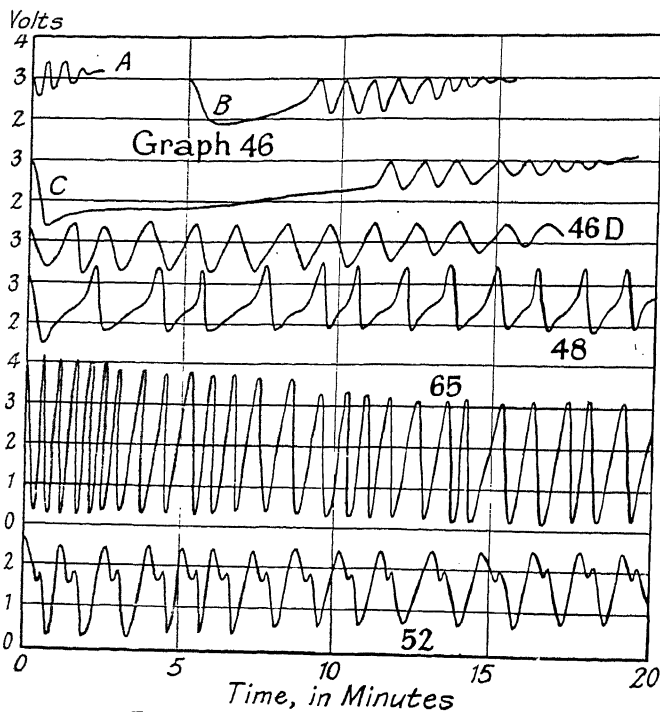
Fig. 17.—Periodic anodic film formation.

potential is reduced to 2·9 volts, B represents a reduction to 2·8 volts, C shows the effect of reducing the potential to 2·7 volts, and D records well-developed oscillations obtained by reducing it to 2·3 volts. In general, the further the potential is reduced in the direction of H (Graph 50) the slower is the damping of the oscillations, whilst systems represented between

E and J are rapidly damped. The longer series are preceded
by an induction period (not plotted in Graph 46D). The critical
current density required to produce the film increases with
rise of temperature and is a linear function of the concentra-
tion of solution between 4 and 16 per cent. (Graph 49, Fig. 16).
These facts point to the accumulation of some product at the
anode as the main condition responsible for the phenomena,
but more definite evidence on this point was obtained later
by conducting experiments with rotating anodes.

In 16 per cent. sodium hydroxide solution the same series
of events occurs, but the oscillations taking place within the
corresponding region of periodicity are continuous instead of
damped. They may continue for many hours. The differ-
ence is doubtless due to the superior solubility of zinc oxide in
the more concentrated alkaline solution. The limits between
which the periods are to be observed are also much wider.
An example of these continuous waves is shown by Graph
48 (Fig. 17).

At the critical current density a white film, probably of
zinc oxide, travels up the metal and the potential rises. Almost
immediately the film turns brown, oxygen is evolved, and
the potential rises still further. Eventually the film becomes
black. This film was observed by E. Newbery (*J.C.S.*, 1916,
109, 1073), who promised an investigation of its nature. It
may be simply zinc oxide, for it is readily soluble in acids
and alkalis, and zinc oxide is known to pass into a brown form
under certain conditions.

A study of Graph 50 (Fig. 16) shows that the production
of periods depends on reducing the potential to just below
the point of incipient oxygen evolution. The line GLE is
almost equipotential with C. In 8 per cent. solutions the film

remains on the anode throughout the periods and oxygen is evolved just at the peaks of the waves. In 16 per cent. solutions, at the peaks of the waves where evolution of oxygen occurs, the film is thrown off into the solution and a fresh film forms at the lower value of potential. The electrode only preserves its metallic surface below the point represented by I, where a sudden drop in the potential occurs. The oscillation, then, is not between the states represented by AB and C′D, as in the experiments with copper, but is, in this case, between the states BC and CC′. This explains why the periods are obtained by reduction from a high voltage rather than by progressive increase in current density. The periods are formed by carefully setting the system in the state represented by the point C, where it has equal opportunities of existing in the state CC′ or CB ; but the point C cannot be reached from below, for the film sets in at B and the potential rises rapidly.

A special feature arising from the consideration of these observations is that the change in the manner of dissolution of the zinc anode brought about at high current densities involves two definite stages. This is important, because similar phenomena have been observed with anodes of other metals, and the observations are in agreement with Müller's differentiation of " Bedeckungspassivität " and " chemische Passivität." The observations tend to show that the first change consists in the formation of a thick, loosely adherent and non-protective film of zinc oxide, which covers most of the electrode surface, raising the effective current density at the exposed parts. Under the influence of the high current density, a thin, invisible and protective oxide film grows, spreading under the thick, loose film, and the oxygen then evolved at the surface of the protective film pushes the initial, loose film off the

electrode. The term " protective " is used in a relative sense, for the zinc continues to dissolve slowly and all the current is not devoted to liberation of oxygen. The phenomena are more definite in electrodes of iron, nickel, and cobalt.

A study was also made of the behaviour of anodes of zinc in sulphuric acid solutions. In 100 per cent. and 90 per cent. sulphuric acid practically no current would pass, owing to the formation of an insoluble film of zinc sulphate. In 60 and 50 per cent. solutions the sulphate film readily formed over the electrode, the potential rising to a high value and oxygen being evolved. With solutions below 35 per cent. the preliminary reaction of the zinc with the acid was very energetic, and no film was formed on the electrode over the range of current densities employed. In very dilute solutions (below 2 per cent.) an oxide film formed on the electrode at high current densities, but this was loosely adherent and did not appreciably affect the strength of the current.

Periodic phenomena were realised in solutions containing 40 to 45 per cent. of sulphuric acid. In a 42 per cent. solution at a current density of 142 milliamps. per cm.^{2} a white film swept up the metal, the potential rising to 3·3 volts. On reducing the potential slightly, continuous oscillations commenced ; an example of these, having an amplitude of 2 volts, is given in Graph 52 (Fig. 17). A visible sign of the periodicity is the evolution of oxygen every time the potential reaches its highest value.

In dilute solutions of hydrochloric acid at very high current densities a dark grey film formed on the zinc anode, but did not affect the passage of current ; in dilute nitric acid solutions a non-adherent, white, flaky substance fell continuously from the anode at high current densities ; and in

dilute solutions of ammonium chloride, ammonium sulphate, or sodium nitrate loose, gelatinous, zinc hydroxide fell continuously from the anode even at fairly low current densities.

Cadmium Anodes.

In sodium hydroxide solutions a brown film formed over a cadmium anode at quite low current densities. Cadmium oxide is not soluble in sodium hydroxide solution and periodic film formation is not to be expected.

In sulphuric acid solutions containing more than 60 per cent. an insoluble sulphate film readily formed over the electrode, and no film formed at the current densities used in solutions weaker than 20 per cent. Periodic phenomena were observed in solutions containing between 25 and 35 per cent. of sulphuric acid. In 30 per cent. sulphuric acid a white film formed over the cadmium when the current density was raised to 108 milliamps. per cm.^{2} and the potential difference rose from 0·3 to 12·0 volts, oxygen being evolved. The potential difference was then reduced to 4·0 volts and continuous periods of large amplitude followed. An example in which the potential difference oscillated between 0 and 3 to 4 volts is given in Graph 65 (Fig. 17). Evolution of oxygen occurred at the peaks of the waves.

In potassium cyanide solutions a cadmium anode behaved in a way similar to that described for a zinc anode in sodium hydroxide solutions, dissolving as the double cyanide at low current densities, with formation of an oxide film at higher current densities and providing also an intermediate, oscillating state. In dilute solutions of hydrochloric or nitric acid (2 and 1 per cent.) a white, flaky substance fell continuously from the anode at elevated current densities.

Mercury Anodes.

The redistilled mercury used in these experiments was contained in a small glass cup of the type used in the ordinary mercury voltameter, connexion being made by means of a platinum wire, fused through the glass. A special feature of film formation on mercury is the concomitant change in surface tension; when the film forms periodically, the mercury surface is alternately flattened and elevated.

In 10 per cent. potassium cyanide solution, electrolysed with a potential difference of 2·0 volts, a black film formed over the mercury anode after an interval of 15 minutes, and continued to dissolve and form again periodically at intervals of 10 seconds. The upper limit of the region of periodicity is 3·5 volts, above which the film is permanent. The reaction is probably due to the discharge of hydroxyl ions with dissolution of the mercurous oxide by the potassium cyanide. Similar effects were noted in 10 per cent. sodium hydrosulphide solutions.

In 10 and 5 per cent. nitric acid solutions a yellow, basic mercurous nitrate formed at the mercury surface at a certain critical current density. In a 40 per cent. solution a grey, crystalline film, probably of mercurous nitrate, formed at high current densities. In 25 per cent. nitric acid at a current density of 20 milliamps. per cm.^{2} a grey film formed and the mercury surface pulsated rapidly and continuously.

In solutions of hydrochloric or sulphuric acid insoluble films of mercurous chloride or sulphate formed at the lowest current densities; in 8 per cent. sodium hydroxide solution a yellow oxide film formed on the electrode and oxygen was evolved.

Magnesium Anodes.

A highly resistant film formed immediately on magnesium anodes in sulphuric acid solutions of concentration 70 per cent. and above, the potential rising to a high value. The metal was observed to assume a peculiarly bright lustre and on breaking the current the high-potential state persisted. The metal continues to dissolve slowly when in this state and the passivity is probably due to a film of magnesium sulphate. In solutions containing less than 50 per cent. of sulphuric acid, magnesium dissolved with great vigour and the surface remained dull. Only in 65 per cent. solutions was any periodic effect observed. With a current density of 50 milliamps. per cm.² the potential difference rose suddenly to 5·0 volts. On reducing it slowly to 1·8 volts, slow oscillations between 1·2 and 1·5 volts followed.

In this group of elements, therefore, the limits of periodicity in sulphuric acid solution are defined by the following concentrations : magnesium, 65 per cent. ; zinc, 45 to 40 per cent. ; cadmium 35 to 25 per cent. ; mercury, nil. There is thus a correspondence between the concentration range and the solubility of the sulphate.

Tin Anodes.

In sulphuric acid solution the phenomena observed were in every respect similar to those with zinc and cadmium electrodes. Periods were produced only in 5 per cent. solution, where, with a current density of 175 milliamps. per cm.² a white film formed over the anode, the potential rising from 1·7 to 4·4 volts. After the lapse of a second or so, evolution of oxygen commenced and the potential rose further to 5·7 volts.

By reducing to 3·5 volts, continuous oscillations between 2·2 and 3·2 volts followed, having a period of one minute.

In solutions of nitric acid more concentrated than 40 per cent. the preliminary reaction of the tin was extremely vigorous, giving a voluminous product of hydrated stannic oxide. In 100 per cent. nitric acid, once the reaction had started, a current density of approximately 10,000 milliamps. per cm.^{2} was required to form a coherent film of oxide, which stopped further action even when the circuit was broken. In solutions weaker than 20 per cent. a grey substance (probably a mixture of stannic and stannous oxides) fell continuously from the anode. Periodic phenomena were observed in 1 and 0·5 per cent. solutions. In the former case a black film formed over the anode at a current density of 30 milliamps. per cm.^{2} and the potential difference rose from 1·1 to 1·6 volts. By reducing it to 1·3 volts continuous oscillations between 1·1 and 1·5 volts followed.

Lead Anodes.

The behaviour of lead as an anode is truly saturnine, all changes in potential being exceedingly sluggish and sometimes taking 10 minutes for completion. In general, it seems that a slowly-forming film does not exhibit periodic phenomena. Lead was not examined in much detail, but the electrochemical behaviour of lead is important in the study of the lead accumulator.

Iron Anodes.

Particular interest is attached to the behaviour of iron as an anode, the phenomena of passivity being more definite than with any of the metals described so far. A more detailed

examination has therefore been made (Hedges, *J.C.S.*, 1926, 2878).

In solutions containing more than 60 per cent. of sulphuric acid a low current density was sufficient to cause the potential to rise to a high value, oxygen being evolved. The whitish appearance of the anode suggested the formation of a film of anhydrous ferrous sulphate. In a 40 per cent. solution at a current density of 160 milliamps. per cm.^{2} the potential difference rose from 1·2 to 3·2 volts and oxygen was evolved, the potential oscillating continuously thereafter between 1·1 and 3·3 volts, in periods of 50 seconds. Hydrogen was evolved at the lower potential ; this ceased as the potential rose and then gave place to evolution of oxygen ; during the next fall of potential the oxygen evolution ceased and slow evolution of hydrogen was reinstated. Immediately before the evolution of oxygen a white film could be observed to sweep up the anode. The iron was permanently in the passive state at current densities greater than 250 milliamps. per cm.^{2} and permanently active when the current density was below 160 milliamps. per cm.^{2}

If the iron was removed from the solution when in its high-potential state, the high potential persisted on plunging it back again ; but if in the meantime the iron was dipped into water it was found to be active on plunging it back into the electrolyte. These observations suggested that in these solutions the iron becomes enveloped in a resistant film of ferrous sulphate, which is much less soluble in strong solutions of sulphuric acid than in water. It was found also that the passivity obtained in the 100, 80 and 60 per cent. solutions was removable by immersing the electrode in water. The conclusion agrees with that reached independently by Müller.

In more dilute solutions of sulphuric acid the passivity appears to be quite different. In 10 and 5 per cent. solutions great difficulty was experienced in inducing passivity, and it was found best to complete the circuit before immersing the anode, so that the initial current density was very high. With a current density of 420 milliamps. per cm.^{2}, in 10 per cent. sulphuric acid the potential difference oscillated continuously between 1·5 and 3·3 volts, in periods of 40 seconds. No gas was evolved during the active state of the metal, but evolution of oxygen occurred while the metal was in the passive state. In this case, however, the metal was lustrous during the passive periods, but acquired a dull, dark grey film during the active periods. Each time passivity set in the film peeled off, and subsequently dissolved in the solution. Evolution of oxygen then ensued, beginning at the lowest part of the electrode, up which the passive state rapidly travelled until the whole of the metal was evolving oxygen. At the end of the period, the oxygen evolution ceased and the metal slowly acquired its grey film, which again peeled off at the next period of oxygen evolution.

In 5 per cent. sulphuric acid solution, continuous oscillations between 2·4 and 4·0 volts, having a period of 30 seconds, were obtained with a current density of 850 milliamps. per cm.^{2} The film in this case did not peel off during each period, but apparently dissolved, uncovering the lustrous surface. Closer observation showed that the film is completed just before the potential rises, then oxygen is evolved, and the film disappears.

In nitric acid (d 1·42) the iron became passive before the current was started. In a 90 per cent. solution the reaction was very vigorous, but the metal could be rendered passive

by adopting the device described for the more dilute sulphuric acid solutions ; passivity then spread from the first point of contact over the whole electrode, and the metal remained passive on breaking the circuit. Periodic passivity occurred in 40 and 20 per cent. solutions, the potential oscillating between 1·6 and 3·4 volts. The metal had a brown-coloured surface at the low potential and was bright during the passive periods, when oxygen was evolved. The current density used for the 20 per cent. solution was 1800 milliamps. per cm.^{2}, and the periods succeeded each other at intervals of 10 seconds. In 10, 2, and 1 per cent. solutions passivation took place more readily, but did not become periodic.

Periodic film formation and the corresponding electrical changes were also observed with iron anodes in solutions of orthophosphoric acid. In solutions of sodium hydroxide or potassium cyanide iron became passive at the lowest current densities, whilst in hydrochloric acid solutions the highest available current density did not induce the passive state. In solutions of ammonium sulphate or sodium sulphate the main product was ferrous hydroxide, which fell continuously from the anode, but at higher current densities permanent passivity set in.

Cobalt Anodes.

A brown film readily formed over a cobalt anode in 100 and 80 per cent. sulphuric acid, and oxygen was evolved. Periodicity was observed in solutions containing from 1 to 50 per cent. and the effect was far more striking than in the corresponding experiments with iron. The effects produced vary to some extent with the concentration.

In a 50 per cent. solution, cobaltous sulphate was formed

below 70 milliamps. per cm.^{2}.   Immediately this value of current density was reached, however, the potential difference rose from 1·2 to 2·6 volts, and continued to oscillate in regular periods of about 1 second between these values, oxygen being evolved at the high potential.   The periodicity was observed over a wide range, but above a current density of 250 milliamps. per cm.^{2} the cobalt remained permanently in the passive state, oxygen being evolved continuously.   The cobalt continued to dissolve when in the passive state, but formed a dark green solution of cobaltic sulphate.   The surface of the metal appeared black throughout.   The green colour did not appear in solutions less concentrated than this.

Solutions containing 20 or 15 per cent. of sulphuric acid were best for observing changes in the state of the electrode, which correspond exactly with those recorded for iron.   At the end of each passive period, during which the cobalt was lustrous, evolution of oxygen ceased and the surface of the metal became dull ; immediately before the next passive period a dark grey film travelled up the anode and peeled off as the evolution of oxygen began afresh.

In solutions of hydrochloric acid, nitric acid, ammonium sulphate, and sodium sulphate at the concentrations examined, a cobalt anode did not become passive ; on the other hand, in 8 per cent. sodium hydroxide and in 20 per cent. potassium cyanide it became passive immediately and remained so after the circuit had been broken.

Nickel Anodes.

The behaviour of nickel in sulphuric acid solutions was similar to that of iron and cobalt.   In 100 and 80 per cent. solutions the potential soon rose to a high value, due to

the formation of difficultly soluble nickel sulphate. Periodic passivity was observed over the concentration range 60 to 5 per cent. The effect was less striking than in the foregoing instances, however, the amplitude being generally of the order of 0·2 volt. As in the previous cases, oxygen was evolved during the passive periods and a dark film travelled up the metal immediately prior to its becoming passive.

In solutions of hydrochloric acid and of ammonium chloride the anode remained active at all current densities. Solutions of sodium hydroxide and of potassium cyanide caused passivity immediately, and ammonium sulphate produced the passive state very readily. Periodic phenomena were not encountered in these systems.

Aluminium Anodes.

An anode of aluminium in 100 per cent. nitric acid dissolved continuously at low current densities, but at 50 milliamps. per cm.^{2} the potential difference oscillated regularly between 1·2 volts and 14·0 volts in periods of 20 seconds. Gas was evolved slowly during these periods, but the surface of the electrode appeared to be unchanged. If a very thin oxide film had formed periodically, however, it would probably have escaped observation, being transparent.

In 8 per cent. sodium hydroxide solution an aluminium anode dissolved smoothly at moderate current densities, hydrogen being evolved simultaneously when the current was sufficiently low. Evolution of hydrogen ceased when 60 milliamps. per cm.^{2} was reached. At 70 milliamps. per cm.^{2} a brass-coloured film appeared on the anode, and at 75 milliamps. per cm.^{2} the potential oscillated in regular periods of 25 seconds between 1·65 and 2·0 volts, and a few bubbles, presumably

of oxygen, were evolved. Above 110 milliamps. per cm.^{2} the potential remained constant. When a very small anode was employed, giving a current density of the order of 10,000 milliamps. per cm.^{2}, vigorous evolution of oxygen occurred and the metal remained bright.

The Conditions for Periodicity and Passivity.

The experiments which have just been outlined have involved the examination of a large number of electrolytic systems, and from this exhaustive study it is possible to define some of the conditions necessary to secure periodic effects. (1) A film must form over the anode. (2) This film must be soluble in the electrolyte when the circuit is broken. It follows that the electrode may exist in one of two possible states—with or without the film. (3) The current density must be between two well-defined limits, which depend on the temperature, concentration, and composition of the solution. Periodic phenomena can be realised by so arranging the current density that the electrode has almost equal chances of remaining in one state or passing into the other. The result is that the electrode oscillates continuously between these two states. The region over which this periodic effect can be observed is often very narrow, but sometimes (particularly in the case of copper in hydrochloric acid) is quite extensive.

The experiments also tend to show that periodic passivity is simply a special case, for it seems that periodicity ensues wherever the anode is given simultaneous opportunities of existing in the active or passive state. In order to test this point further, special experiments were devised in which a passive anode was progressively activated, the idea being that at some stage, when activity and passivity were almost

equally probable, the system would alternate continuously between the two states.

The progressive activation was effected in three ways : (a) by raising the temperature of the system; (b) by dilution of the reagent; (c) by the addition of some agent favouring the active state.

(a) The system aluminium—100 per cent. nitric acid was used. At 20° C. passivity readily set in and was permanent. At 30° the periods described on page 159 were produced. At 40° the system still alternated between the two states, but very rapidly, the amplitude being only from 1·0 to 7·0 volts. At 60° the aluminium remained active.

(b) The same system was taken and 0·5 c.c. of water was added to the nitric acid at 20°. Still the passivity was permanent when it developed. Further small additions of water were made until 2 c.c. had been added ; oscillations between 1·7 and 13·4 volts with a 30-second period were then produced. An excess of water caused the aluminium to become completely active. In the experiments at 20°, a white, gelatinous, transparent film peeled off the anode ; in one case, the solution was allowed to become warm and this film apparently dissolved in the acid at the higher temperature.

(c) A nickel anode immediately becomes passive in 5 per cent. ammonium sulphate solution, as shown by the steep portion of Curve 1 (Fig. 18), where potential is plotted against current density; on the other hand, it remains active in 5 per cent. ammonium chloride solution (Curve 6, Fig. 18). The behaviour of a nickel anode was examined in ammonium sulphate solutions containing progressively increasing quantities of ammonium chloride, in the expectation that a state would be reached at which the activating and passivating

influences balance each other, so that the electrode would alternate continually from one state to the other.

The results were as expected and are shown in Curves 2, 3, 4, and 5 (Fig. 18). The effect of adding 0·1 per cent. of ammonium chloride to the 5 per cent. ammonium sulphate is depicted by Curve 2, which shows that passivation occurs, but there is a shift in the direction of the active state. The
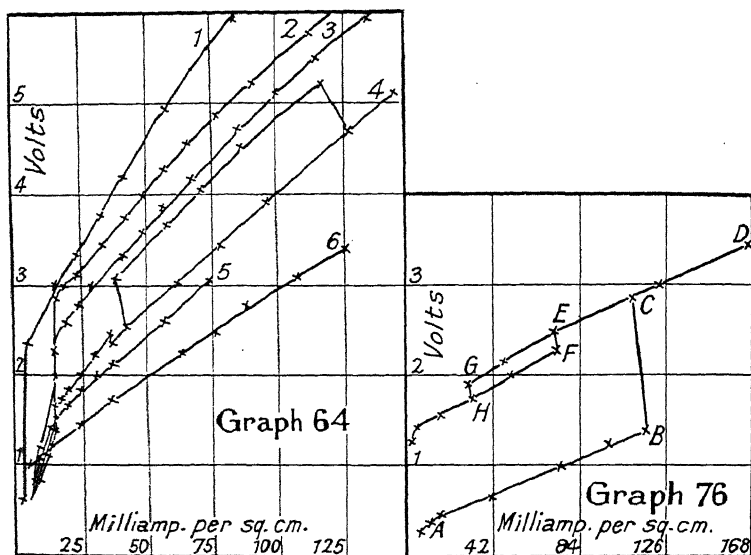
FIG. 18.—Effect of chlorine ions on the passivation of a nickel anode.

FIG. 19.—Current density-potential curve for nickel in dilute sulphuric acid.

addition of 0·2 per cent. of ammonium chloride is represented by Curve 3; here the degree of passivation is still less. In the presence of 0·5 per cent. of ammonium chloride (Curve 4), passivation occurs to a smaller extent, but at a current density of 38 milliamps. per cm.² the nickel becomes active once more. Between this value and 125 milliamps. per cm.² the anode alternates regularly between the active and passive states in

periods of 5 to 10 seconds with an amplitude having a mean value of 0·6 volt. These limits of periodicity are represented in the graph by the quadrilateral. At current densities greater than 125 milliamps. per cm.^{2} the nickel became permanently active. An equally good region of periodicity (not shown in the graph) was found when the solution contained 0·3 per cent. of ammonium chloride. The solution containing 1·0 per cent. of ammonium chloride is beyond the region of periodicity, the nickel remaining active throughout (Curve 5).

The following table records the values of potential difference for a given current density of 50 milliamps. per cm.^{2} with progressive increase in the amount of ammonium chloride. It illustrates the region of periodicity lying on the border-line between two states :—

Solution.			Potential.
5 % $(NH_4)_2SO_4$			4·6
,,	$\div$ 0·1 % NH_4Cl		4·0
,,	$\div$ 0·2 %	,,	3·65
,,	$\div$ 0·3 %	,,	3·4 $\rightleftharpoons$ 2·8
,,	$\div$ 0·5 %	,,	3·4 $\rightleftharpoons$ 2·8
,,	$\div$ 1·0 %	,,	2·5
5 % NH_4Cl			2·05

It appears, therefore, that the limits of periodicity at the anode are defined by exactly the same conditions for film formation as for what is regarded as passivity in the narrower sense. It may be concluded that passivity in the narrower sense is a special case of film formation, in which the film is characterised by highly protective properties. Such a film is bound to be exceedingly thin and may be expected to be invisible under normal conditions.

The analogy between metals which become passive in the narrower sense (nickel) and those which become " pseudo-

passive '' (zinc) at high current densities is strikingly illus-
trated by Fig. 19. This is a current density-potential curve
for a nickel anode in 5 per cent. sulphuric acid and should be
compared with Fig. 16 (p. 146), which is a similar curve for
a zinc anode in sodium hydroxide solution. The line AB
represents the rise of potential with increasing current density
until the point represented by B is reached. At this critical
current density the nickel becomes passive (or the zinc becomes
enveloped in a film) and the potential rises to C, oxygen being
evolved. Further increase of current causes the potential to
rise along the line CD. When the current is reduced, the
potential retraces the same path to C, but continues as far as
E. If the current density is reduced to values represented
between G and E, the potential oscillates continuously between
two values defined by the area EGHF, oxygen being evolved
intermittently.

It is true that the nickel anode dissolves extremely slowly
when passive, whereas the zinc in a similar state dissolves
relatively rapidly, but that seems to be only a matter of degree—
a change in the ratio of current employed in liberating oxygen
to the current used in forming ions of the metal—which varies
from metal to metal in any case.

On the other hand, the experiments show that " true "
passivity is immediately preceded by the formation of a visible
film, which disappears at the moment the electrode assumes
the passive state ; an observation also made by Müller. It
will be recalled, further, that in the experiments with a zinc
anode in concentrated sodium hydroxide solutions the film
was flung from the metal each time oxygen was evolved, and
it formed over the metal during the periods of lower potential.

There is thus a large amount of evidence which suggests

that passivity is a general property exhibited to various extents by all metals under suitable conditions. All the evidence appears to support the conclusion that passivity produced by anodic polarisation and by purely chemical means is the same phenomenon, that it is the result of the formation of a film of insoluble material, and that it is exhibited to different degrees depending on the protective properties of the film *under the particular conditions prevailing*.

The Mechanism of Anodic Polarisation.

From the work which has been described, Hedges (*J.C.S.*, 1928, 969) has developed the following theory of anodic polarisation. When an iron anode is dissolving in dilute sulphuric acid, there will be a certain critical current density above which sulphate ions are discharged more quickly than they can be replaced by diffusion. At this point some hydroxyl ions will be discharged simultaneously. In addition, since hydrogen ions are repelled from the positively charged anode, the hydroxyl-ion concentration in the layer of liquid immediately contiguous to the anode will increase. The net result of these effects is the production of oxide or basic salt at the surface of the anode. Since sulphate ions are still being discharged, the film will not be continuous and thus, in virtue of its non-protective nature, will attain visible thickness. The relatively thick film will have the effect, however, of raising very greatly the effective current density at those areas of the electrode left uncovered. Consequently, at some isolated spots the discharge will consist mainly of hydroxyl ions, giving a perfectly continuous oxide film. Once this protective film has formed, it is immaterial whether sulphate ions or hydroxyl ions are discharged at its surface, for either will produce evolution of

oxygen. Although the thin, invisible film cannot then grow in thickness, it will extend sideways, rapidly covering the whole electrode. At this stage, oxygen will be evolved at the surface of the *invisible* film, causing the discontinuous *visible* film to be thrown off the electrode.

This view is supported by experiments which have been carried out on the influence of speed of rotation of the anode on periodic electrochemical passivity and which are described in the next section.

The theory is of general applicability to other metals such as zinc or copper, which do not become passive in the narrower sense, but nevertheless at high current densities undergo an increased potential and become enveloped in a visible film, for it is a question of the varying degrees of protection afforded by the film. The truly passive behaviour of an iron anode will be attained only when the production of a highly protective, and therefore thin and invisible, film is possible. In other cases this state will be approached to a greater or less extent, giving in each case a different ratio of current employed in forming ions of the metal and in producing oxygen. The existence of periodic activity and passivity under constant external application of current shows that the protection offered even by the so-called " protective " film is not permanent.

These views receive confirmation from some later work by Evans (*Nature*, 1930, **126**, 130), who has now isolated the film responsible for the passivity of an iron anode in dilute sulphuric acid by alternately making and breaking the circuit. The film is in optical contact with the metal during the passive stage, and becomes visible under the microscope when the metal immediately below it is dissolved away during the active stage. The film is mechanically flimsy, but stable chemically,

and can survive for an hour in normal sulphuric acid. Whilst the direct solvent action of dilute sulphuric acid on isolated ferric oxide films is very slow, the relatively rapid removal of a ferric oxide film from an iron base in the ordinary way by acid is due to the formation of the local cell iron acid ferric oxide, in which the ferric oxide is reduced cathodically to the rapidly soluble ferrous oxide. If the whole surface receives anodic treatment, this cathodic reduction is prevented ; hence, an iron anode may remain passive in acid solution.

Experiments with a Rotating Anode.

In an endeavour further to elucidate the mechanism of periodic anodic film formation and passivity, some experiments were carried out with rotating anodes (Hedges, *J.C.S.*, 1929, 1028). The system chosen for investigation was the anodic dissolution of copper in hydrochloric acid, since this gives an effect of the greatest magnitude. Instead of measuring the total potential difference across the electrolytic cell, the potential difference between the anode alone and a normal calomel electrode was determined. Further, the measurements were made by a string electrometer. This method has the advantage that absolutely no current is taken from the system, and the instrument is entirely dead-beat and can be used for following very rapid vibrations.

A striking result from the experiments with a rotating copper anode in hydrochloric acid is that the frequency of the periods is independent of current density over a certain range and later decreases almost linearly with increasing current density. This is shown by Graph 101 (Fig. 20), in which the frequency (number of waves per second $\times$ 100) has been plotted against the current density. The system represented

is a copper anode in 25 per cent. hydrochloric acid and each
curve refers to a different speed of rotation, varying between
240 and 1200 r.p.m.   The graphs shows (1) that the critical
current density for periodicity increases with speed of rotation,
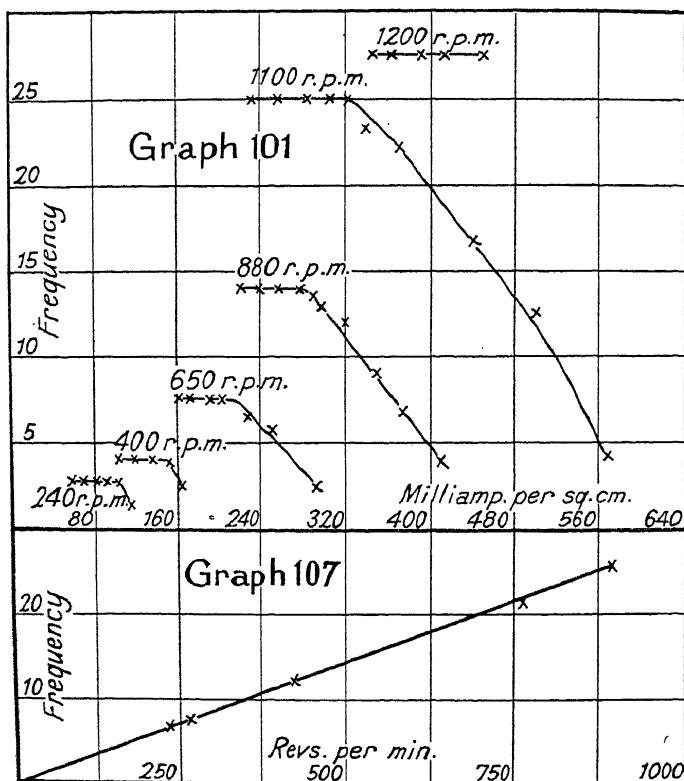
Fig. 20.—Influence of speed of rotation of the anode on periodic
film formation.

(2) that there is a "characteristic frequency," independent
of current density and increasing with speed of rotation, and
(3) that a second critical current density exists, at which the
frequency ceases to be independent of current density and
which also rises with speed of rotation.

The existence of a characteristic frequency, independent of current density and increasing with the speed of rotation, indicates at once that the frequency is not dependent on the rate at which metal ions leave the electrode. That the phenomenon is quite independent of the velocity of dissolution of a metal is confirmed by other work on the periodic formation of films at an unattackable anode (Hedges, *J.C.S.*, 1926, 2591).

The most probable interpretation of the second part of each curve, where frequency decreases with increasing current density, is that at a sufficiently high current density some product begins to accumulate on the anode. Until this second critical current density is reached, the rotation is rapid enough to wash away the product as fast as it is formed. The rise of the second critical current density with increasing speed of rotation is consistent with this view. It will be shown later that the product concerned is cuprous chloride.

Graph 107 (Fig. 20) shows the relation between frequency and speed of rotation for a copper anode in 40 per cent. hydrochloric acid. This graph was made by determining the frequency-current density curve for each speed and then plotting the " characteristic frequency " against the speed. The points lie on a straight line passing through the origin. It appears, therefore, that the frequency is independent of the rate of dissolution of the anode, but is in direct proportion to the speed of rotation. The graph indicates that one complete period is produced for every fifty-eight revolutions (approximately) of the electrode, independently of the rate of revolution.

Variation of the speed of rotation can produce two effects : (1) the anodic product is washed away more rapidly ; (2) chloride ions are supplied to the anode at a greater rate. If the

frequency were determined by the first of these effects, it would not be independent of current density ; consequently, it may be inferred that the frequency is controlled by the rate of supply of chloride ions to the anode.

Apart from variation in the speed of rotation, the rate of supply of chloride ions to the anode can be varied by altering the concentration of the hydrochloric acid. Experiments
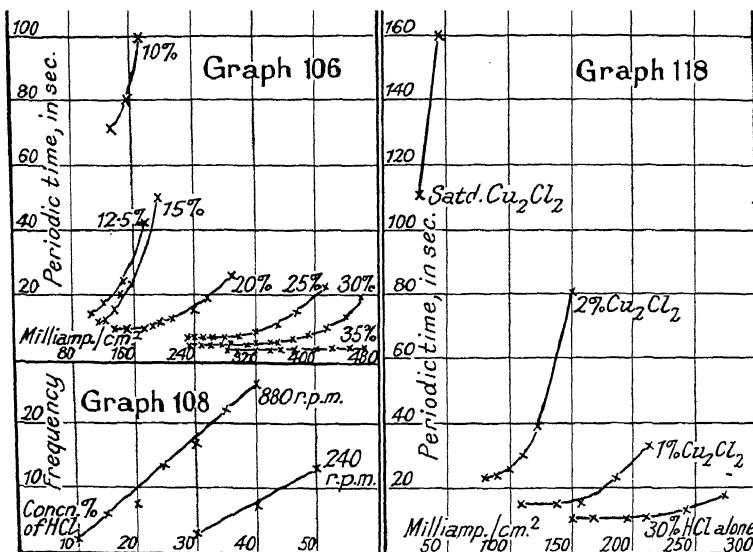
FIG. 21.—Influence of concentration of acid on periodic anodic phenomena.

FIG. 22.—Influence of cuprous chloride on the anodic dissolution of copper.

were carried out with solutions of hydrochloric acid varying in concentration between 10 and 40 per cent., a constant speed of 880 r.p.m. being used, and the results are shown in Graph 106 (Fig. 21). Instead of plotting the frequency, its reciprocal —the " periodic time," or duration of a period in seconds —has been plotted against the current density. As expected from the considerations given above, both the critical current

density required to produce the periods and the characteristic frequency increase with the concentration of acid. The graph also shows that the independence between frequency (or periodic time) and current density is not realised in solutions of hydrochloric acid containing less than 20 per cent. and that the region of independence is more marked the higher the concentration. This suggests that the product responsible for the change of frequency with current density at low speeds and low concentrations is cuprous chloride, which is far more readily soluble in the concentrated acid. Some experiments were conducted, therefore, in which 1 per cent., 2 per cent., or an excess of cuprous chloride was added directly to the system, consisting of a copper anode rotating at 880 r.p.m. in 30 per cent. hydrochloric acid, and the results are represented by Graph 118 (Fig. 22). With increasing amounts of cuprous chloride, both the critical current density required to produce periods and the frequency of the periods are lowered, and the horizontal part of the curve, indicating independence between frequency and current density, is destroyed. In fact, Graph 118 is precisely similar to Graph 106, and it may be inferred that cuprous chloride is the responsible product.

The amplitude of the periods obtained with a rotating anode is, in general, less than that of the periods with a stationary anode. The amplitude is about 1 volt during the stage where frequency is independent of current density, but increases considerably after the second critical current density has been passed. With a stationary anode, amplitudes of about 12 volts were recorded. This suggests that when cuprous chloride begins to collect at the anode, a much thicker oxide film is produced—probably by hydrolysis of the cuprous chloride.

If the frequency is determined by the rate of supply of

chloride ions to the anode, a linear relation between frequency and concentration of hydrochloric acid is to be expected. That this is realised is shown by Graph 108 (Fig. 21), where the characteristic frequency is plotted against concentration for two different speeds, 880 and 240 r.p.m. The points were obtained by determining the frequency-current density curve for each concentration, and plotting the value of the frequency corresponding to the horizontal portion of the curve.

The experiments indicate that the frequency of the periods is independent of the current density, but proportional to the rate of stirring and to the concentration of the acid. Three factors can be concerned in determining the frequency : (1) rate of removal of ions from the metal, (2) rate of removal of anodic product, (3) rate of supply of chloride ions to the anode. Since (1) and (2) are dependent on the current density, it may be inferred that the rate of diffusion of chloride ions is the controlling factor. The distinction between (1) and (3) holds only at these high current densities considered, *i.e.* above the critical current density. At low current densities it is not possible to distinguish between (1) and (3), but at high current densities negative ions other than chloride (*e.g.* hydroxyl) compete ; the rate of supply of chloride ions is determined by the stirring, and the rate of ionisation of the metal is determined by the current density.

The following view of the mechanism has been developed. At low current densities cuprous chloride is formed at the anode ; this, being soluble in the acid solution, is washed away from the anode continuously, and fresh chloride ions diffuse in continuously. The potential therefore remains constant at a low value. It is to be noted that in the formation

of the cuprous chloride-hydrochloric acid complex the chloride ions are removed, as such, from the sphere of action. At a certain critical current density the rate of disposal of chloride ions begins to overtake the rate of diffusion of fresh chloride ions to the electrode. This produces two effects : (a) the scarcity of chloride ions in the layer of liquid immediately contiguous to the anode allows hydroxyl ions to be discharged, and (b) hydrogen ions migrate away from the positively charged anode. The effect (b) tends to make the layer of liquid alkaline. The discharge of hydroxyl ions (a) makes the anolyte as a whole more acid, but the hydrogen ions so produced migrate from the vicinity of the electrode according to (b). It is necessary to distinguish between this thin, alkaline liquid sheath and the anolyte as a whole, which, of course, tends to become more acid. The thin, alkaline sheath is of greater importance in considering the behaviour of the anode. Both effects (a) and (b) have the same result—the formation of an oxidic film (basic salt or oxide) on the metal, (a) by direct discharge of hydroxyl ions, or (b) by hydrolysis of the primary anodic product. This film, which is visible, explains the rise in potential, or passivity in its widest sense.

In the case of the easily passivated metals, such as iron, the visible film reduces the active area of the electrode, raising enormously the effective current density at the uncovered spots, so that an invisible, highly protective oxide film forms at these points and rapidly spreads to cover the entire electrode according to the mechanism suggested on page 165.

The subsequent fall of potential is due to the action of the hydrochloric acid on the oxidic film, changing it to cuprous chloride, which subsequently dissolves in the acid. This change is easily visible, and its direction of propagation over the

electrode always follows the direction of flow of the hydro-
chloric acid, which can be varied at will. It is easy to see that
after the fall of potential, the original current density being
reinstated, the oxidic film will form again. The fundamental
problem is why the dissolution of the film takes place in defi-
nite periods instead of there being set up a state of dynamic
equilibrium. The experiments showing that the frequency
of the periods depends entirely on the rate of accumulation
of chloride ions appear to leave no escape from the conclusion
that dissolution of the film does not occur until a certain critical
concentration is reached, but that when reaction occurs in
each " pulse " it is complete. This is analogous to the " all-
or-nothing " law so familiar in physiology, according to which
a system does not respond to a stimulus until this reaches a
threshold value, but the response is complete when that value
is reached. The second part of the requirement corresponds
with the fact that, once the breakdown of the protective film
has been initiated at some point, the change will spread over
the entire electrode in the way studied by Lillie (see p. 109).

Periodic phenomena in electrolysis are encountered only
between certain well-defined border-line conditions, and the
idea of a critical concentration of some ion required to effect
the change of the electrode from one state to the other is capable
of extension to all the systems examined, both at the anode and
at the cathode. Indeed, experiments on the periodic electro-
deposition of metals through secondary reaction (Hedges,
J.C.S., 1927, 1077) afford strong independent support for the
view, and are difficult to explain in any other way. Physiolo-
gists use a similar view to explain the periodicity of breathing ;
respiration occurs every time the carbon dioxide content
(hydrogen-ion concentration) of the blood reaches a threshold

value. Although the older idea, that the heart-beat is caused by alternate reaction with or absorption of calcium and potassium ions, does not appear to be greatly favoured by physiologists, it may be pointed out that analogous mechanisms do exist. For example, in the electrolysis of potassium mercuricyanide solutions, under certain conditions the potassium liberated at the mercury cathode reacts alternately with water molecules and with the complex $Hg(CN)_4''$ ions or undissociated salt, the effect being a periodic evolution of hydrogen alternating with deposition of mercury. The supposition here is that reaction of potassium with the complex ions does not take place until the ions reach a certain critical concentration by diffusion.

One experimental result appears to contradict the theory that has been developed. The temperature coefficient of the periods given by a rotating copper anode in 40 per cent. hydrochloric acid, determined by measuring the frequency at $30°$ and at $40°$, was found to be $1·8$ per $10°$—a high value if the frequency is controlled entirely by a diffusion process. However, the difficulty of interpreting the temperature coefficient of a complicated series of chemical and physical processes is well known.

Critical Concentrations in Activation.

If the fall of potential and dissolution of the film are due to the hydrochloric acid slowly reaching a critical concentration by diffusion in the neighbourhood of the anode, it should be possible to produce the same effect by adding hydrochloric acid directly to a permanently " passive " anode. This has been done. A copper anode was rotated at 120 r.p.m. in 15 per cent. hydrochloric acid, a current density of 300 milliamps.

per cm.² being used. The film soon appeared and the current density fell to 147 milliamps. per cm.², at which it remained constant, for the high current density is above the region of periodicity, the film remaining permanently. Hydrochloric acid was added in small quantities at a time to the stirred liquid, and the amount of current passing was read after each addition. In Graph 119 (Fig. 23) the total current is plotted inversely against the number of c.c. of hydrochloric acid. The gradual addition of hydrochloric acid causes a slow fall in potential
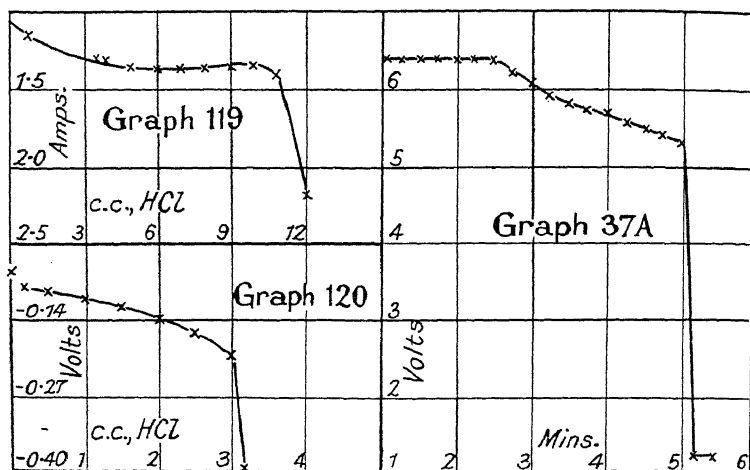
FIG. 23.—Activation by critical concentrations of ions.

until a certain critical concentration is reached, whereupon the fall becomes sudden. That this artificial process is identical with that occurring spontaneously in the periodic dissolution is evident from a comparison of Graph 119 with Graph 37A (Fig. 23), which shows the manner of fall of potential during one period.

Further evidence has been sought in the change from passive to active iron, the passivity being produced by purely chemical means. A strip of electrolytic iron was rotated

at 180 r.p.m. in concentrated nitric acid and successive small quantities of hydrochloric acid were added at intervals. After each addition the potential against a normal calomel electrode was measured. The results are plotted in Graph 120 (Fig. 23) and show that here also activation occurs suddenly when a certain critical concentration of chloride ions is reached.

It would not be correct to attach any special significance to the value of the critical concentration required to effect the change in any given instance, for *both passivity and activation depend on the protective properties of the film under the particular conditions prevailing.*

L. McCulloch (*Trans. Amer. Electrochem. Soc.*, 1929, **56,** 325) has suggested that since iron and nickel give anhydrous sulphates which go into solution slowly, these substances may compose the films which cause the passivity of anodes of these metals in sulphuric acid. Suggestions along these lines were made by Hedges to explain passivity in the more concentrated sulphuric acid solutions, but can scarcely be regarded as having a wider applicability.

Optical Investigation of Anodic Passivity.

The optical method used by Freundlich and his collaborators for the investigation of the passivity of iron mirrors in nitric acid and in air (see p. 98) has been applied to the examination of anodic passivity by L. Tronstad (*Nature*, 1929, **124,** 373 ; *Z. physikal. Chem.*, 1929, **142,** 1 ; *Det Kgl. Norske Videnskabers Selskabs Skrifter*, 1931, No. 1). The state of polarisation of light reflected from mirrors of iron and nickel rendered passive and active in various electrolyte solutions was examined. The important point was established, not only that the optical constants of nickel and iron rendered passive in

sodium hydroxide solution and nickel rendered passive in sulphuric acid solution undergo a change, but that the change in optical properties resembles that observed when a clean iron surface is brought from a vacuum into contact with air. This points directly to the formation of an oxide film during anodic passivation.

When iron and nickel are rendered passive by anodic polarisation in alkaline solution the optical properties tend towards a characteristic limiting value. When the anode is subsequently activated the optical properties change in the opposite sense, but even on prolonged activation the initial value is never reached. By repeatedly making the metal active and passive, greater changes take place in the optical properties than by keeping the metal in the passive state for a long period. This behaviour is explained by supposing that the oxide film is not totally destroyed on activation, but becomes porous ; on re-passivation the holes are refilled with oxide and the films become thicker.

The mechanism by which it is suggested that the oxide film is formed involves hydrolysis in the layer of liquid in the immediate vicinity of the anode and is almost identical with the views of Hedges. It is further pointed out, however, that the substance of the film is negatively charged and will be held tightly to the anode by cataphoresis.

Technical Significance.

Anodic passivity is a matter of some importance in the electro-refining and electroplating industries, for when an anode becomes passive the electrical energy is utilised in performing chemical processes other than those desired. In

addition, the composition of the bath may change through the anode ceasing to dissolve.

The work which has been discussed renders it clear that the chances of passivation are reduced by any process which tends to supply fresh electrolyte to the anode and to remove the anodic products. Every effort should be made, therefore, to ensure a good circulation of liquid round the anodes, by assisting convexion through so placing the anodes that the products can fall away, by avoiding " pockets " in the neighbourhood of the electrodes, or by stirring the electrolyte or moving the electrodes. The study of the activating effects of different ions should also prove useful, indicating that the addition of chlorides to a bath, where possible, will reduce the probability of passivation of the anode, whilst passivation is favoured by the presence of oxidising anions.

Passivity is also reduced by the superimposition of an alternating current, which, by its alternation of oxidising and reducing conditions, has the effect of making the film thicker and less protective. S. A. Tucker and H. G. Loesch (*Ind. Eng. Chem.*, 1917, **9**, 841) have shown the importance of this in nickel-plating. A. J. Allmand and V. S. Puri (*Trans. Faraday Soc.*, 1925, **21**, 1) have shown that the superimposition of an alternating current on a direct current enables the dissolution of a gold anode, whilst an iron anode may be made to dissolve in dilute sodium hydroxide by the same device (*ibid.*, 1926, **22**, 34).

CHAPTER VII.

PRACTICAL APPLICATIONS OF OXIDE AND SIMILAR FILMS.

THE principles discussed in the preceding chapters have already been applied to some extent to the production of protective coatings of insoluble compounds on some of the commoner metals. In certain cases these coatings serve more for the purpose of decoration than as a serious preventive of corrosion, but where both these aims are served, they are almost ideal. In other cases, oxide and other films of a like nature are applied as a basis for a coating of paint or other material, which adheres better to the treated surface than to an ordinary metal surface. On the whole, films of these compounds have not such lasting protective qualities as are obtained by applying coatings of other metals, nor is their useful range of conditions so wide. Nevertheless, whilst on the one hand the metal-colourer's art is concerned mainly with ornamentation, on the other hand the same principle is involved in the production of stainless steels and other corrosion-resisting alloys; and even the films produced by metal-colouring confer some degree of protection from corrosion, especially when incorporated with oil or lacquer.

Protection of Iron.

Numerous processes are in vogue for reducing corrosion by producing a uniform film of oxide over the surface of the

iron. One of these is sometimes effective in reducing the amount of corrosion of iron and steel in aqueous solutions, such as natural waters, and consists in adding to the water an inhibitive chemical agent. This is generally an alkaline substance (sodium hydroxide, carbonate, silicate, etc.) or a mild oxidising agent (potassium chromate), which acts by forming a protective film of oxide on the surface of the metal in the way described in Chapter III.

The " blueing " of iron may be effected by various oxidising means, such as by heating in the air, or by dipping in fused potassium nitrate, but the oxide film produced thereby is not very protective unless afterwards incorporated with oil. The Bower-Barff process produces a protective coating of magnetic iron oxide by exposing the iron articles to superheated steam at 900° C. and afterwards to coal-gas. Other methods employ boiling solutions of alkaline oxidising agents, and anodic treatment in alkali has also been recommended.

Recently, case-hardening by nitrogen has developed. The steel is heated in ammonia, or, in another process, in fused sodium cyanide, and acquires a surface film of nitride, which, although added for the purpose of producing a very hard surface, also has protective properties. The action may be considered as a type of cementation, a general process which will be described in Chapter XI.

The Coslettising process (T. W. Coslett, *Eng. Pat.* 8667, April, 1906) consists in immersing iron articles in a solution of phosphoric acid saturated with ferrous phosphate. The phosphate film formed is very protective, even when quite thin, and has a slate colour. It is not particularly ornamental, but when covered with a layer of enamel offers remarkably good protection against atmospheric corrosion.

Parkerising produces a phosphate film by immersing the iron articles in a boiling solution containing 25 grams of phosphoric acid and 1·5 grams of manganese dioxide per litre. After 2 to 4 hours the articles have acquired a dark grey coat and are rinsed in water and dried in sawdust. Particles of sawdust are removed by brushing and the article is heated until water dropped upon it is instantly thrown off. At this temperature the article is immersed in linseed oil, removed, drained, and gently heated to dryness.

S. Field and S. R. Bonney ("The Chemical Coloring of Metals," Chapman & Hall, 1925) recommend a solution containing 150 grams of calcium hydrogen phosphate in a litre. The articles are immersed in the boiling solution until a slaty colour is attained, and are then removed, rinsed with cold water, then with hot water, and finally dried in sawdust. The dried articles are immersed in a heavy oil, which is kept at about 100° C. for an hour.

The stainless steels, which owe their corrosion-resisting properties to the possession of a continuous, spontaneously acquired and self-healing film of oxide, will be discussed in a separate section.

Protection of Aluminium.

Early attempts were made by R. Seligman and P. Williams (*J. Inst. Metals*, 1920, **23**, 169) to augment the natural oxide film on aluminium. Amongst the methods found to be more or less effective were heating the metal, immersing in ammonia and in solutions of sodium phosphate and bicarbonate. Although aluminium sheets so treated showed enhanced resistance to corrosion, this resistance is broken down whenever the corrosive properties of the water are increased. Treating the water

with chromates or nitrates was found to be an effective means of preventing pitting of aluminium.

In a further paper, Seligman and Williams (*ibid.*, 1923, 28, 297) have studied the cleaning of aluminium utensils by means of soda. Although soda solutions rapidly dissolve aluminium, it was found that they no longer do so in the presence of a relatively small quantity of sodium silicate. The mixture can safely be used, therefore, for cleaning aluminium articles. It is probable that a protective film of aluminium silicate is formed.

The increasing use of aluminium and its alloys in aircraft, and particularly in marine aircraft, has made the protection of aluminium against corrosion by the atmosphere and by sea-water a matter of importance.

The Jirotka process confers a protective film on the surface of aluminium and certain of its alloys by immersing in a bath containing an aqueous solution of chromates and salts of heavy metals, kept at a moderate temperature.

The Stafford O'Brien process consists of anodic treatment at low voltage in sulphuric acid containing a chloride. The process is claimed to be effective not only with aluminium, but with its alloys, including the high-copper alloys.

A method of protecting aluminium which has received world-wide application is the anodic oxidation process due to G. D. Bengough and J. M. Stuart (*Eng. Pat.* 223994, Aug., 1923). This process consists in making the article to be treated the anode in a bath containing 3 per cent. aqueous chromic acid solution, the voltage being raised gradually from zero to 40 volts in 15 minutes, maintained at 40 volts for 35 minutes, raised to 50 volts in the course of 5 minutes and maintained at 50 volts for a further 5 minutes.

For the practical operation of the process, appropriate motor-generators with means of obtaining the desired regulation of voltage have proved the most convenient. Steel tanks have been used extensively as containers, and plates of graphite or of stainless steel have proved satisfactory for cathodes, where a minimum reduction of the chromic acid is desired. As will be expected, the presence of chlorides in the bath is very undesirable, as they lead to breakdown of the protective film ; it has also been found beneficial to keep the sulphate content as low as possible.

The anodic process can be applied to aluminium, Duralumin, and most aluminium alloys, but alloys containing more than 5 per cent. of copper have not proved capable of being treated. Duralumin, Y-alloy, and similar alloys can be treated equally well, whether in the finally heat-treated and aged condition or after softening treatment. Pieces can also be heat-treated after the anodic treatment, provided reasonable care is taken to avoid scratching the film.

The protective film is produced uniformly over all parts of the surface accessible to the electrolyte, and the " throwing power " is excellent, deep recesses receiving a coating equal to that on the outstanding parts. The treatment of commercial aluminium sheet requires a current density of 2·8 to 3·6 amps. per sq. ft. ; the current consumption varies with the nature of the surface of the metal, being higher for rough than for smooth surfaces.

As W. Rosenhain (*J. Inst. Metals*, 1928, **38,** 267) has pointed out, a great advantage that the anodic oxidation process has over other methods of coating is that it automatically completes itself. When the current drops to a very low standard value there can no longer be any uncoated areas, for such areas would carry the current.

The protection against corrosion afforded by the anodic film is improved by the subsequent application of suitable paints, enamel, or grease. Lanoline has been widely used for the purpose. The ungreased film may be dyed by immersing in aqueous solutions of dyes for which aluminium hydroxide is a suitable mordant, and thus artistically coloured and corrosion-resisting aluminium products may be obtained (Bengough and Stuart, *Eng. Pat.* 223995, Aug., 1923).

Protection of Magnesium.

A recent development, which seems to offer opportunities for increasing application in the future, is the use of light magnesium alloys in aircraft construction. It is clearly important to protect such material against corrosion by the atmosphere and by sea-water.

Attempts to produce a film having the requisite properties by anodic oxidation have not yet proved successful. A method which gives an improved resistance to corrosion (*Eng. Pat.* 287450) consists in dipping the magnesium or alloy in a hot, concentrated solution of potassium dichromate, containing about 15 per cent. of concentrated nitric acid. A golden film is produced on the metal. The treatment is rather drastic, and a considerable amount of metal is necessarily lost through the violence of the preliminary reaction.

The method recommended by Sutton, Sidery, Le Brocq and Braithwaite (*Eng. Pat.* 331853) is to immerse the magnesium for some hours in a neutral or alkaline solution of alkali chromate or dichromate, containing an aluminium salt. The film produced is further protected by lacquer or lanoline.

L. Whitby (*J. Soc. Chem. Ind.*, 1931, **50**, 83T) has utilised the passivating action of chromic acid on magnesium by

devising a method of removing the corrosion products without appreciably affecting the metal. A boiling 20 per cent. solution of chromic acid is recommended ; the magnesium is rendered passive thereby and the amount of dissolution may be neglected, whilst the corrosion products dissolve. The presence of chloride in the corrosion products has an activating influence, but the effect may be inhibited by the addition of a small amount of silver chromate to the chromic acid.

Further researches of Whitby (*Eng. Pat.* 14724, May, 1931) have led to a promising means of protecting magnesium, for which a patent has recently been taken out. The method is simple and consists in immersing the metal in a solution of sodium selenite, preferably in the presence of a small amount of acid. The conditions are not narrowly fixed, and the concentration, temperature, and acidity of the solution may be varied over a wide range. The process appears to be one of simple reduction, a film of elementary selenium forming over the surface of the magnesium.

Protection of Copper.

A " red " copper is produced by the Japanese and owes its resistance to corrosion to an oxide film. The material appears to be obtained by casting copper on canvas under water and then exposing the mass to the action of steam. The colouring is said to last indefinitely.

The work of Vernon, showing that the green patina which forms on copper exposed to the open air consists mainly of basic copper sulphate, has been described on page 89, where it was also stated that the film has excellent protective properties. An interesting development of this work is a patent (Vernon, *Eng. Pat.* 14723, May, 1931) covering a method

of protecting copper and its alloys by artificially producing a green patina which resembles that formed naturally. The natural formation of the patina requires a period of many years, but the artificial method aims at producing it in a short time. The article to be coloured is treated several times with a solution of ammonium sulphate (about 10 per cent.) and then with a solution of copper sulphate (about 10 per cent.) to which has been added about 1 per cent. of sodium hydroxide or other alkaline hydroxide or carbonate, and optionally about 5 per cent. of ammonium nitrate. Satisfactory results have been obtained by applying the ammonium sulphate solution twice daily for a week, followed by two days' treatment with the copper sulphate solution. During treatment the specimen is freely exposed to the air, but is protected from the sun during hot weather. No further treatment is required before the treated specimen is finally exposed to the air. The treatment is particularly successful when applied to arsenical copper. The usual method of application is by brushing, but spraying or other methods may be used.

Stainless Steels.

The corrosion-resisting properties of the stainless or rustless steels are connected in the first instance with the presence of chromium in the steel. That such materials are not really chemically inert, but owe their properties to the possession of an oxide film of exceptional protective power, appears from some work by Y. Utida and M. Saito (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, **13**, 391). They found that certain alloys of iron, chromium, and nickel increased in weight on oxidation, rapidly in the initial stages, almost imperceptibly after half an hour, reaching a practically constant value after another hour

or so. This is the behaviour which has come to be recognised as characteristic of reactions involving the formation of protective films.

Chromium becomes passive more readily than iron and confers this property on steel when alloyed with it, the general resistance of a steel increasing with the chromium content. This fact has been established by N. B. Pilling and D. E. Ackerman (*Trans. Amer. Inst. Min. Met. Eng.*, 1929, Tech. Publ. No. 174), who determined the concentration of nitric acid required to produce passivity in iron-nickel-chromium alloys of various compositions. That the usual phenomena of passivity are involved is also indicated by the observation by A. Krüger (*Chem. Ztg.*, 1931, **55**, 335), that chromium steel, whilst attacked by hot, dilute acid solutions, is perfectly resistant to boiling solutions of sodium hydroxide.

The isolation by Evans (see Chapter III.) of a transparent film on stainless steel has given the fullest confirmation to these views. The film isolated was considerably thinner than that on ordinary iron, indicating a very highly protective value. No doubt the fact that ferric and chromic oxides form a continuous series of solid solutions may be considered in part explanation of why chromium is a suitable addition in the production of rustless steels. The relatively greater tendency of chromium to become passive not only imparts to the alloy the ability to acquire an oxide film having highly protective properties, but the film is self-healing, even by exposure to the atmosphere, if accidentally injured. This is a matter in which stainless steels have a great advantage over all types of artificially applied coatings ; the artificial films are always subject to accidental damage, even if their normal wearing properties are sufficiently good, but the film on stainless

steel is of the natural, spontaneously acquired type and keeps in repair automatically.

As previously mentioned, protective films tend to become unstable at phase boundaries, and the homogeneity of the metal is an important point in ensuring continuity of the film. In order to understand fully the corrosion-resistant properties of stainless steels it is necessary, therefore, to describe briefly the effect of the additions on the constitution of steel, especially as modified by heat-treatment. An excellent review of this subject has been given by Carpenter (*J. Roy. Soc. Arts.*, 1931, **79,** 557).

Steel solidifies as a solid solution of carbon in iron, and this solid solution at 1000° C. is known as austenite. When cooled further, transformations occur resulting in two constituents : (*a*) ferrite, which is pure iron, and (*b*) pearlite, which is composed of alternate plates of ferrite and cementite (a carbide Fe_3C). The relative amounts of the constituents depend on the carbon content of the steel ; the heterogeneous mixture formed during cooling causes carbon steel to corrode more readily than pure iron.

The " critical range," or range of temperature in which austenite transforms to ferrite and pearlite varies with the carbon content ; in carbon steels it is about 900° to 700° C. The changes may be prevented by rapid cooling, however, and when carbon steel is quenched in water, ferrite and pearlite are not produced. At the ordinary temperature another change occurs ; the iron changes to some extent from the γ to the α state with the carbon still in solution. The rate of cooling required to suppress the normal transformation and retain austenite unchanged is very important and is diminished by the addition of chromium, nickel, manganese, or

molybdenum. The addition of chromium to steel raises the temperature at which the changes on heating begin, reduces the amount of carbon required to form pearlite, and retards the solution of carbon during heating. J. H. C. Monypenny (*J. Iron and Steel Inst.*, 1920, 493) states that steel containing 12 per cent. of chromium consists entirely of pearlite when the carbon content is as low as 0·3 per cent. ; the constitution is similar, therefore, to a carbon steel containing 0·9 per cent. of carbon. For this reason the carbon content of stainless steels is generally limited to 0·3 per cent., for higher proportions result in free cementite being formed.

In steels containing only carbon and chromium the austenitic type is not produced. Nickel is an important constituent of certain types of stainless steel ; it lowers the transformation temperatures, and if a sufficient quantity is added austenite may be retained at the ordinary temperature. The usual kinds of austenitic stainless steels contain from 7 to 14 per cent. of nickel and from 15 to 20 per cent. of chromium. " Anka " steel contains 11 per cent. of nickel and 15 per cent. of chromium, " Staybrite " steel contains 8 per cent. of nickel and 18 per cent. of chromium, and V . 2A steel contains 7 per cent. of nickel and 20 per cent. of chromium. If these steels are heated for a time between 600° and 900° C. a certain amount of α-iron and carbide is produced, to the detriment of their corrosion-resistant properties.

It must be remembered that the mechanical properties of stainless steels have to be considered simultaneously with their corrosion-resisting properties. Steels which are martensitic (the α-solid solution) after quenching are fairly homogeneous although not to the extent of the austenitic steels. They are very hard, and although tempering softens them it also destroys

their uniformity and reduces their resistance to corrosion. If the same resistance to corrosion is required in a tempered steel as that observed in the steel when quenched, either the carbon-content must be reduced or the chromium-content increased.

Low-Carbon Stainless Steel.

This class, which is the stainless equivalent of ordinary mild steel, contains 0·07 to 0·12 per cent. of carbon and 8·6 to 12 per cent. of chromium. The most usual composition is about 0·1 per cent. of carbon and 11 or 12 per cent. of chromium. The best resistance to corrosion is developed when quenched and is not seriously impaired by tempering below 500° C. Tempering above this temperature reduces the resistance to corrosion, however, owing to the formation of carbide particles. When the chromium content of these low-carbon steels is increased to 14 per cent. they are stainless when annealed, and may be cold-worked without the resistance breaking down, thus having an advantage over the 0·3 per cent. carbon steels. Stainless steels of the low-carbon type are used for purposes where malleability is a distinct advantage in addition to immunity to corrosion. They are employed in the manufacture of spoons, forks, etc., and for turbine blades.

Stainless Steel for Cutlery.

This type of stainless steel contains about 0·3 per cent. of carbon and 11 to 14 per cent. of chromium. In this system the carbide is not completely dissolved until a temperature of at least 1000° C. is reached, and quenching from at least this temperature is necessary in order to develop maximum

resistance to corrosion ; otherwise, the particles of carbide destroy the continuity of the protective film. In practice, the usual quenching temperature is about 950° C., because articles quenched from the higher temperature are liable to break. When the steel is annealed by cooling from above the critical range at a rate which permits the formation of pearlite, its resistance to corrosion is at a minimum ; this type of steel also suffers from the disadvantage that severe cold working lowers the resistance to corrosion.

Apart from cutlery, this grade of stainless steel is used in a variety of other industries, and has found application in surgical instruments, pumps, locomotives, and in the handling of many chemical products and food-stuffs.

High-Chromium Steels.

Increasing the chromium content above 16 per cent. has the effect of imparting a higher resistance to corrosion, and steels containing more than 18 per cent. of chromium find many applications, especially where resistance to oxidation at high temperatures is required. The properties of such high-chromium steels (containing sometimes more than 30 per cent. of chromium) are described by C. E. McQuigg (*Trans. Amer. Inst. Min. Met. Eng.*, 1923).

Austenitic Stainless Steels.

By the addition of nickel to chromium steels the range of stability of austenite is greatly increased, so that this solid solution may be retained at the ordinary temperature. Leaving aside the variations which can be produced in mechanical properties, the austenitic nickel-chromium steels have a better general resistance to corrosion than the other varieties ; this

resistance is not destroyed by cold working, and they have a high resistance to oxidation at elevated temperatures. These steels have a very wide range of application in civil, mechanical, and mining engineering, in the handling and transportation of acids and other chemicals, in shop fittings, bathroom fittings, and numerous domestic appliances.

Metal-Colouring.

The colouring of metals is carried out with the object of increasing the æsthetic value of the work, or to give the appearance of age to new materials, but changed economic and psychological conditions have also played a part in increasing the demand for coloured metals for domestic purposes. In domestic service many metals acquire a surface patina which, although often attractive in the early stages, generally leads to a dirty or dull appearance in time. Time was when such metallic surfaces were religiously kept polished and pride was taken in their brightness ; nowadays, it is more usual to prefer an " oxidised " finish to the metal, which fixes the patina at some pleasing stage of its development and does away with the work of cleaning.

The films produced for these purposes are not as a rule particularly resistant to corrosion, but are made so (for ordinary, domestic purposes) by adding a coat of lacquer or by incorporating oil or grease in the film after its application. When this is done, the film definitely has more than æsthetic value, for it acts as a porous body, which tenaciously retains the final protective coating in a way which would not be possible on a clean metallic surface. A lacquer applied directly to a metal tends to peel, whereas a film of oxide or sulphide at the surface acts as a bond between the two. An " oxidised "

finish forms an excellent ground-work for a final protective coating.

Nevertheless, an increased protective power of the "oxidised" film itself would be of great value, and it seems that there is room for serious research on these lines. Vernon (*British Non-Ferrous Metals Research Association :* Research Report, No. 4, p. 7) has pointed out that whilst oxide films on copper act in a protective way, sulphide films actually promote further attack ; and yet sulphide films are used to a greater extent than oxide films for colouring effects. Clearly, the aim should be to produce films which have both a pleasing, artistic appearance and good protective properties. As an example of such a film, reference may be made to the green patina produced artificially on copper, mentioned on page 186. It would probably prove to be of great advantage if metal-colourers and corrosion experts were to work together on this matter ; metal-colouring is generally treated in a purely empirical way.

Field and Bonney ("Chemical Coloring of Metals," Chapman & Hall, 1925) distinguish four general methods for the colouring of metals : (1) Mechanical methods, in which a coloured material is applied to the surface of the metal by some system of dipping, painting, or spraying ; (2) thermal methods, in which the application of heat effects the formation of coloured or colour-producing films ; (3) chemical methods, in which the films are produced by the interaction of the metal with some chemical reagent ; (4) electrolytic methods, in which films of metals, oxides, or other compounds are obtained by electrolytic action. A few examples are given below.

"Oxidised" copper generally owes its finish to a film of cuprous sulphide, applied by immersing the copper in solutions

of various sulphides. A cold solution containing 12·5 grams of potassium sulphide and 200 grams of ammonium chloride in 1 litre of water may be applied by means of a brush or by immersing the article. Rinsing in cold water, then in hot water, and drying in sawdust completes the operations. The colour may vary from light brown to black, and slow production in dilute solutions gives a more adherent deposit. Certain parts of the article are generally relieved by gently rubbing with fine, damp pumice powder applied with a piece of felt, thus giving pleasing effects. Sulphides of barium, ammonium, and other metals are also used for various effects, the technique varying in the different cases.

An oxide finish on brass is produced by immersing the article in a 2·5 per cent. solution of copper sulphate to which ammonia has been added in amount just insufficient to prevent entire re-dissolution of the precipitated hydroxide. A black film is produced in a few seconds and is fixed by rinsing in water and dipping quickly in a solution containing 1·6 per cent. of sodium hydroxide. The film may be relieved in parts, if desired, by dry scratch-brushing and then preserved by lacquering. A finish resembling steel may be made on brass by immersing in a solution of arsenious chloride, preferably containing some ammonium chloride.

" Oxidised " silver owes its colour to a film of silver sulphide, produced by immersing the article in solutions of soluble sulphides, such as the sulphides of ammonium, potassium, or barium, or by the action of hydrogen sulphide. When the film has formed, the article is rinsed in water, dried, and relieved according to taste. Sand-blasting with various grades of sand produces different types of matt surfaces.

An interesting decorative effect, used to advantage on toys

is made by depositing anodically a thin film of lead peroxide on a polished metal surface. If the cathode is a wire, placed so as to present only a point to the anode, the distribution of current density is such that the film deposited is thickest at a point on the anode opposite to the cathode and becomes progressively thinner along radii travelling out from this point. The effect of such a progressively thinning film is to give a series of rainbow tints (Nobili's rings).

CHAPTER VIII.

COATING BY HOT–DIPPING.

THE coating of metals with a film of another metal, both as a means of reducing corrosion and for purposes of ornamentation, has been practised for some centuries. An excellent account of this subject is given in H. S. Rawdon's " Protective Metallic Coatings " (Chemical Catalog Co., New York), from which some of the details given here have been taken. In the following chapters an account of the different methods in vogue will be given. The oldest method, which is still the basis of a very large industry, consists of dipping the article to be coated in a bath of molten metal and after a sufficient time removing it with its adherent film of metal. This method is known as " hot-dipping."

Certain features are essential for the process to be a success commercially. The metal which forms the coating should have a relatively low melting-point, for not only does immersion in a bath at an elevated temperature alter considerably the mechanical properties of the base metal, but most metals have a distinct solubility in each other, which at high temperatures may be a source of concern. A pronounced solubility of the base metal in the molten metal not only leads to loss of base metal but to a change in the composition of the bath, and in addition there is the penetration of the molten metal into the base metal with formation of an alloy, the properties of which may not be those of the coating desired. The hot-dipping process is therefore more suitable for metals of relatively low melting-point, such as zinc, tin, and lead, whilst coatings of

silver, nickel, copper, and other metals of higher melting-point are preferably effected in other ways.

The alloying action to which reference has been made is an essential feature of the hot-dipping process. When a substance such as sulphur is dipped in water and withdrawn the adherent water is not uniformly distributed over the surface and can readily be shaken off, but when a piece of a water-soluble substance is immersed it is found that on withdrawal a uniform film of solution adheres to the material. This film can be made exceedingly tenuous, and it is in fact a matter of difficulty to remove completely the film of water. This same principle holds in the production of metallic coatings. Not only is a thin film generally desired for both economical and mechanical reasons, but above all the film must be uniform and continuous, for a metal which is badly coated in this re-spect may suffer more local corrosion than a metal which has not been coated. The formation of the alloy layer at the sur-face of the metal ensures the continuity of the film.

In the coating of iron with zinc or tin the alloy layer forms very readily, but in other instances of hot-dipping the alloy is not formed under the conditions of operation. In such cases it is often the custom to add a small quantity of a third metal, which alloys readily with both the base metal and the coating metal. In general, in a hot-dipped metal there is a transition layer of alloy between the base metal and the outer layer of coating metal, but it should be pointed out that the formation of the alloy is not absolutely necessary and that in some in-stances satisfactory metallic coatings may be obtained by hot-dipping in the absence of a transition layer of alloy, provided that the surface of the base metal is perfectly clean and is easily wetted by the molten metal. When an alloy layer is formed

there is the added advantage that the metal coat shows no ten-
dency to draw away from the base when it solidifies. Indeed,
when through any cause subsequent peeling does occur it is
the outer layer that peels off, leaving the alloy layer intact.

A necessary preliminary to the production of a metal
film which is uniformly adherent to the base is the thorough
cleaning of the surface of the base metal, and this is important
not only for hot-dipping but also equally for all other metal-
coating processes. Grease and oxide scale are the chief
contaminating substances which have to be removed, and the
methods employed vary with the nature of the base metal and
with other factors. Grease may be removed by means of
solvents such as benzene or carbon tetrachloride or by treat-
ment with hot alkali solutions, or by an electrolytic cleansing
method, making the article the cathode of a cell in which an
alkaline solution is used as the electrolyte. Cathodic treat-
ment also serves to remove oxide scale, the evolution of hydrogen
bubbles breaking up the scale mechanically, whilst in some
cases reduction of the oxide to the metal also occurs. The
scale is sometimes removed by purely mechanical means, such
as wire-brushing or sand-blasting, but the more usual method
is to remove it by treatment with acids—a process which is
termed " pickling."

When a metal such as iron covered with a scale of oxide
is immersed in dilute sulphuric or hydrochloric acid the iron
is attacked and hydrogen is evolved. The acid penetrates
between the iron and the scale and loosens the latter, the pro-
cess being helped very materially by the disengagement of
hydrogen ; the iron scale is not readily soluble in acids and its
removal is thus mechanically effected by severing its connexion
with the underlying metal. In other cases the oxide may be

more easily attacked by the acid than is the metal. In order to reduce the amount of dissolution of the iron in the pickling of scaled sheet, colloidal materials are sometimes added to the pickling bath. Colloids retard very considerably the rate of dissolution of metals in acids (Hedges, " Colloids," Arnold & Co., 1931, p. 243).

In the pickling of steel sheets which are to be coated with zinc, the sheets are supported by a basket of a resistant alloy such as aluminium bronze or Monel metal, and are immersed in a warm 7 per cent. sulphuric acid solution, which is kept in motion in order to assist the removal of the scale as it becomes loosened by the action of the acid. The temperature is maintained by means of heating coils through which steam is passed. When the pickling operation is over the sheets are washed in water and stored therein until they are used ; immediately before the coating operation they are pickled in dilute hydrochloric acid, which removes any rust. Hydrochloric acid dissolves most metallic oxides more readily than sulphuric acid does.

An unsatisfactory feature inherent in the hot-dipping process is the difficult task of regulating the thickness of the coating, a matter of great economic importance. In general, hot-dipped coatings are thicker than metallic coatings obtained by other methods. In certain cases, such as the dipping of wire or sheet, which is performed entirely mechanically, the excess of molten metal can be wiped off by asbestos wipers and the approximate thickness of the remaining film is then fixed, but with small objects this is not generally possible and there is no universal method of regulating the thickness of the coating. Sometimes the excess of metal is removed by centrifuging.

Zinc Coatings.

That the corrosion of iron can be allayed by an outer coating of zinc has been known for a long time, and the application of hot-dipping for this purpose appears to date from experiments made by Melouin in 1741. In 1836 Sorel developed a technique which is essentially the same as that used to-day. The articles were pickled in dilute sulphuric acid, washed in water, pickled in dilute hydrochloric acid, dried, and immersed in a bath of molten zinc covered with a layer of ammonium chloride. On these lines the process has been developed into an industry of importance.

Outline of the Process.

The bath used for the dipping is usually of iron, but trials have been made with refractory material, and may hold upwards of thirty tons of zinc in the molten state. The melting-point of zinc is 419·4° C. and the average working temperature is therefore somewhat higher—about 450° C., but the exact conditions depend to some extent on the nature of the material to be coated. The higher the temperature, the greater is the solvent action of the molten zinc on the walls of the container and the greater is its alloying action on the material which is being dipped. The relative surface area of the material is also important in fixing the optimum temperature. At the temperature of the bath the base metal undergoes some annealing, and the hot-dipping process is therefore not suitable for coating articles such as springs.

Articles of irregular shape, such as structural parts, nuts, bolts, pails, ash-bins, etc., are dipped by hand, but sheets, wire, wire-netting, etc., are conveyed continuously through the bath by machinery. In the case of hand-dipped articles the surface

is rubbed with a wooden spatula just before removal from the bath, and the article if fairly large (*e.g.* a laundry tub) is allowed to drain ; if small (nuts, bolts, etc.), the excess of zinc may be removed by shaking or centrifuging in a machine. The coating on machine-dipped plates can be kept approximately to the desired thickness by adjusting the rollers through which the plates leave the bath, and in the case of wire a wiper of asbestos is often used to remove excess. Apart from the economical significance of removing excess of zinc, the thickness of the coating is of importance, especially in the case of wire or sheet, in that it affects the mechanical properties of the material, particularly on bending. Very severe wiping may remove the free zinc almost entirely, leaving the metal with a very thin coating of zinc-iron alloy.

An average coating for sheet is 1 oz. of zinc per square foot of surface.

The surface of the molten zinc in the bath is covered by a layer of flux, which consists of ammonium chloride with some tallow and occasionally glycerol. The metal is dipped through the flux, but the exit end of the bath is usually not so covered, the flux being bounded by a transverse partition, which extends a few inches below the surface of the molten metal. The flux serves to clean the metal as it enters the bath to remove moisture and to prevent oxidation of the surface layer of zinc. In the coating of wire, the wire is often passed through a solution of zinc chloride and then dried immediately before entering the bath.

The Addition of other Metals and the Effects of Impurities.

Molten zinc has an appreciable solvent action on iron and therefore attacks both the lining of the bath and any iron articles

which are immersed therein. According to the equilibrium diagram of the iron-zinc system given by Pierce (*Trans. Amer. Inst. Min. Met. Eng.*, 1923, **68**, 767), the solubility limit of iron in molten zinc at 450° C. is 0·10 per cent. The bath therefore soon becomes a saturated solution of iron in zinc, and as the iron content of the bath increases crystals of an iron zinc alloy, $FeZn_7$, separate out and fall to the bottom of the bath. The layer of this alloy which forms is referred to as dross. According to Sang (*Rev. mét.*, 1912, **9**, 1, 78, 160, 275), the total iron content of the bath should not be allowed to exceed 0·2 per cent., and in practice it is necessary to remove the dross periodically. Attempts have been made to find irons and steels which are specially resistant to the solvent action of molten zinc, but no great success can be claimed.

W. G. Imhoff (*Amer. Metal Market*, 1929, **36**) has made a study of the effect of the molten zinc on the iron container. The corrosion of the container is mild up to 482° C., but is violent above that temperature. The rate of dissolution of iron and steel in molten zinc increases directly in proportion to the amount of impurities and increases with the amount of oxygen. A study of different steels showed that the purer the steel the less soluble it is, chromium and nickel steels being more readily dissolved.

The zinc slabs which are fed into the bath generally contain a certain amount of lead. Zinc and lead are only slightly miscible in the molten state, and the lead therefore forms a separate layer at the bottom of the bath. In some cases, lead is intentionally added to the bath ; it forms a layer on which the iron-zinc dross floats and thus enables its more ready removal, and in addition it prevents overheating of the bottom of the container and so diminishes the attack on the iron and reduces the amount of dross formed.

For some purposes aluminium in the form of a zinc-aluminium alloy is added to the bath. The addition of 0·25 per cent. of aluminium is sufficient to produce a marked effect, rendering the contents of the bath more fluid. This has the result of giving a thinner coating to the objects, but a coating which is more uniform and which is also whiter. The increased fluidity makes the addition of aluminium useful in the coating of small, irregularly-shaped articles, especially those containing crevices.

About 1 per cent. of tin is sometimes added to the bath for the purpose of securing a more uniform coating. The temperature of solidification of the melt is reduced greatly by small amounts of tin, and this fact probably offers an explanation of the effect produced.

The effect of these additions has been discussed mainly from the point of view of their effect on the thickness of the coating, which is an all-important matter if the material has afterwards to be subjected to mechanical deformation. Metals other than zinc in the outer layer may also have a far-reaching effect on the resistance of the protective layer to corrosion. Prost (*Revue universelle des Mines*, 1920, **6,** 353) found that the presence of small amounts of lead, iron, or cadmium in zinc (common impurities) increases the rate of corrosion by acid solutions, and that the addition of antimony, arsenic, copper, or tin has a similar effect.

On the other hand, atmospheric corrosion of the zinc is not affected to the same extent. According to Prost, small amounts of cadmium, lead, iron, tin or arsenic have no appreciable effect on the rate of atmospheric corrosion, but antimony even at a concentration of only 0·03 per cent. accelerates corrosion and a similar amount of copper prevents it. The

behaviour of the products towards atmospheric corrosion is more important than the effect of acids, since zinc-coated materials are not expected to withstand the action of strong acids. On the other hand, accelerated corrosion tests are in some respects more reliable than tests requiring an exposure of several years.

R. Vondraček and J. Izák-Križko (*Rec. trav. chim.*, 1925, **44,** 376) have measured the velocity of dissolution of pure zinc and its alloys in $0.5N$-sulphuric acid by casting the metal into a cylinder, one face of which was ground and left free to be attacked by the acid, and measuring the volume of hydrogen evolved. Mercury and aluminium were found to have a marked lowering influence on the velocity of dissolution. Lead was practically without effect, whilst cadmium, arsenic, tin, antimony, iron, and copper increased the velocity of dissolution in the order given. For alloys of zinc with tin and cadmium the maximum dissolution velocity was scarcely influenced by increasing the content of these metals from 0.5 to 1.0 per cent., whereas, in the case of iron, the increase was almost directly proportional to the iron content over the range 0.01 to 1.23 per cent.

M. Centnerszwer and M. Straumanais (*Z. physikal. Chem.*, 1925, **118,** 415) report that the presence of iron, silver, antimony, bismuth, copper, arsenic, cobalt, gold, and nickel accelerates the rate of dissolution of zinc by acids, whilst a retardation is produced by cadmium, tin, and lead.

Another effect which depends on the presence of other metals in the zinc bath is the " spangle " effect, which is characteristic of hot-dipped zinc coatings. According to an investigation by Hannah and Rhead (*J. Inst. Metals*, 1923, **30,** 79) good spangles cannot be made with pure zinc on iron

or steel and the addition of aluminium or tin does not help. On the other hand, well-developed spangles are produced when the zinc contains lead or bismuth. These authors conclude that the spangle effect is independent of the nature of the steel sheet used, but this appears to be contrary to general practical experience. Occasionally the spangles are absent entirely or over certain areas of a sheet, where the coating has a dull grey appearance. There is some evidence to show that the grey appearance is caused by the retention of hydrogen by the iron during the pickling process. The spangles are much admired and are in general demand, but there is probably little to recommend a spangled coating apart from its appearance. Large spangles are often an indication of a thin coating, and it seems that the zinc film is especially thin near the margins of large spangles.

Structure of the Coating.

Photomicrographs of the zinc-coated iron products reveal the existence of at least two and sometimes three distinct layers. Next to the base metal there is a layer consisting mainly of the intermetallic compound $FeZn_3$; the outer layer is mainly zinc, which is saturated with iron, and there may be an intermediate layer consisting largely of the compound $FeZn_7$. The presence of another metal sometimes has a marked influence on the structure of the coating, the alloy layer being almost completely absent when aluminium has been added to the bath. The alloy layer is exceptionally well developed when the dipping is carried out slowly. Potential measurements show that the alloys are anodic towards iron and therefore assist in protecting the base metal, although they are inferior to pure zinc in this respect. The alloys are brittle,

however, in comparison with zinc, and their presence has an effect on the mechanical properties of the material as a whole. This is particularly noticeable on bending, when the coating shows a tendency to crack and peel. Attempts have been made to improve the mechanical properties by annealing the hot-dipped articles ; this has the effect of increasing the amount of alloy, but at the same time it decreases the stratification and on bending a series of fine cracks is produced rather than a definite flaking.

Tin Coatings.

The tinning of metals is a much older process than the production of zinc coatings, and the art of coating copper vessels with tin reached a high standard in Roman times. The tinning of iron sheet appears to have begun about the 17th century and has developed into an important industry, especially since fruits and other food-stuffs have been canned on a large scale.

Tin has certain special advantages as a protective film, both mechanically and chemically. The film can withstand severe mechanical deformation without serious damage and the metal is very resistant to atmospheric corrosion. The mode of protection is mechanical and not electrochemical, for tin is a nobler metal than iron, and in an electrolyte solution usually becomes a cathode, the iron dissolving anodically. Whilst discontinuities in a film of zinc do not immediately accelerate corrosion of the iron, because the zinc itself corrodes preferentially, discontinuities in a film of tin are more serious, as the exposed iron is likely to become anodic. A uniform and continuous coating of tin is therefore essential and fortunately the properties of tin are such that very thin, uniform films are readily obtained, provided the surface of the

base metal is of the right character.   Another distinct advantage of tin, which has led to its use for lining containers of food-stuffs, is its lack of toxic properties.   Except in small quantities zinc is distinctly toxic, and in various countries there is legislation to prevent the use of zinc in cooking and other utensils.

The Tinning Process.

The essential features are similar to those described for zinc coating by hot-dipping.   The pickled articles are dipped at about 300° C. in a bath of molten tin, which is covered with a layer of palm oil.   In many installations the tinning bath consists of two compartments, the temperature of the first being kept at about 300° C. and that of the second at about 245° C.   Small objects, such as kitchen utensils, are dipped by hand, but sheet is tinned by mechanical dipping. The sheets are conveyed by rollers through a flux of zinc chloride, pass fairly rapidly through the two compartments of the tin bath, and leave through rollers which are immersed in a layer of oil.   The rollers can be set so as to maintain a certain thickness of the coating.   The high temperature of the oil layer causes a slower solidification of the metal and helps to secure a more uniform coating.   The sheets always retain some oil, even after cleaning with bran, unless they are chemically cleaned by alkali or other suitable agents, but the oil film has for some purposes the desirable feature of retarding corrosion.

As with zinc, a certain amount of the molten tin alloys with the iron of the container, and a dross, consisting mainly of the intermetallic compound $FeSn_2$, separates in the bath and collects at the lower part, from which it is removed periodically and smelted in order to reclaim the tin.   The tin used is generally of a high grade of purity and other metals are not

added to the bath as a rule. Normally, the sheets are not spangled after the hot-dipping process, but for ornamental purposes they can be spangled by subsequent etching with dilute hydrochloric acid. Such an etch-pattern is often observed when a tin containing an acid fruit-juice is opened.

The Structure of the Coating.

The films of tin produced commercially are more difficult to examine than those of zinc because the coating is generally thinner. The film of tin on the containers used for canned foods is usually only about 0·0003 cm. thick. By carefully polishing and etching a bent sheet, it has been possible to demonstrate that there is an outer layer of pure tin and an inner layer of a tin-iron alloy. The alloy layer is extremely thin, partly on account of the short duration of the dipping, and its effect on the mechanical properties of the finished material is therefore scarcely appreciable. Electrochemically, the compounds of iron and tin resemble tin in being cathodic towards iron.

For reasons given, the continuity of the film is important. Blisters sometimes form and can generally be traced to hydrogen taken up by the iron during the pickling. A characteristic defect is a series of minute pinholes extending through the coating to the base, and this is perhaps one of the most important points requiring investigation in the industry. Considering the thinness of the layer of tin, its lack of perfect continuity is scarcely surprising, but as the thickness of the film is increased the number of pinholes per unit area does not decrease in the same proportion. The positions of the pinholes can readily be detected by the ferricyanide test, for microscopical examination shows them to be crater-like depressions at the

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bottom of which the base metal is exposed. According to a report in the *Mitt. Materialprüfungsgamt Kaiser Wilhelm Inst. Metallforschung*, 1926, No. 3, 58, the pinholes are caused by the evolution of hydrogen retained by the iron after pickling. This hydrogen is evolved at the temperature of the tin bath and the minute bubbles burst the film of molten metal. It is claimed that the hydrogen is removed by heating the sheets at 100°-200° C. before immersion in the tin bath and that coatings practically free from pinholes are then obtained.

The Food-Canning Industry.

In the canning of food-stuffs the pinhole defect is a serious matter, for the exposed minute area of iron may become anodic and suffer the local type of corrosion, which may end in the container being pierced. It is interesting to note, however, that according to an investigation by C. L. Mantell and W. G. King (*Trans. Amer. Electrochem. Soc.*, 1927, **51,** 40) the polarity of the iron-tin couple may be reversed under certain conditions, due to the ennobling of the iron through the formation of a surface film. In such a case the iron is unattacked and the tin dissolves.

R. H. Lueck and H. T. Blair (*Trans. Amer. Electrochem. Soc.*, 1928, **54,** 257) showed that in acid solutions free from appreciable amounts of oxidising substances the usual electrochemical relations of iron and tin are reversed, tin becoming anodic to iron. This behaviour was ascribed to the high hydrogen-overpotential of tin in comparison with that of iron. If the accumulation of hydrogen on the initially cathodic tin is prevented, no reversal of polarity occurs. An explanation is thus offered, why perforation occurs in tins of certain fruits and not of others.

E. F. Kohman and N. H. Sandborn (*Ind. Eng. Chem.*, 1928, **20**, 76, 1373) noticed a reversal of potential in the tin-iron couple in fruit juices, the tin being cathodic initially, but becoming anodic after a short time. When the two metals were not in contact the iron corroded more rapidly than the tin.

Recently, a valuable report on the corrosion of the tin-plate container by food products has been made by T. N. Morris and J. M. Bryan (*Dept. Sci. Ind. Res.*, Food Investigation Special Report, No. 40, H.M. Stationery Office, 1931). Their experiments, carried out at the Low Temperature Research Station, Cambridge, have confirmed and established the following features of the electrochemical behaviour of the tin-iron couple: (1) The corrosion of the iron member of the couple is decreased to a remarkable degree by contact with tin. (2) Contact with iron increases the rate of corrosion of tin. (3) The total corrosion of the couple is much less than that of a similar area of iron alone. (4) The corrosion of the tin member of the couple increases markedly as the hydrogen-ion concentration of the corroding medium is decreased. This is true whether air is present or not, although in the absence of air there is a tendency for a maximum to be reached between p_H 4 and 5, which corresponds with the conditions existing in the less acid fruits. (5) The iron is the only member of the couple from which hydrogen gas can be liberated; hydrogen produced by dissolution of the tin is evolved from the iron surface.

There is little doubt that the relative freedom, on the whole, from perforation of containers is due to this reversal of polarity, the tin dissolving from a large area, instead of the iron from a minute exposed area. In that case, although the can does not suffer so much, the possible toxic effect of the tin has to be considered. The general impression is that tin has very

little toxic effect, particularly when present in the insoluble form in which it is found in canned foods. Nevertheless, it is desirable to keep the tin-content of the food-stuff as low as possible. The dissolved tin appears to form a protein complex and is found in an insoluble form especially in the seeds of canned raspberries, strawberries, gooseberries, etc. It is stated that in canned rhubarb and beetroot, which contain little protein, most of the tin is in a soluble form.

Certain substances, such as organic bases, have a rapid action on tin. Monomethylamine has been detected in shrimps and rapidly causes perforation of the cans ; this substance seems to disappear when shrimps are preserved on ice for a day or two before packing, and this procedure is now customary. In further protection the cans are lined with parchment paper, when corrosion takes place only at junctions in the paper and at places where it is pressed against the tin.

The examination of perforated cans has shown that the holes may occur near the seams, along scratches, at corrugations, and at pinholes in the tin coating. Perforations are most common with highly-coloured fruits, such as bilberries, blackberries, and red and black cherries. There is evidence of a connexion between the presence of oxygen, or oxidising agents such as anthocyanin pigments, and perforation. The importance of eliminating air from the cans is clearly indicated.

Another source of trouble in the canning industry is the production of " hydrogen swells " or the bulging of the can through the accumulation of hydrogen produced by corrosion. These may be caused by any food-stuff containing organic acids, but it is remarkable that trouble is most frequently caused by products of low acidity, especially fruits in syrup, ranging from about p_H 3·5 to 4·5. Hydrogen swells are marked

in greengages, plums, grape-fruit, red and black cherries, strawberries, rhubarb, etc., but are not usually found in cans containing Californian peaches, pears, apricots, or sour fruits, such as gooseberries and pine-apples.

A surprising feature of both hydrogen-swells and perforations is that lacquered cans appear to give the most trouble. Acid-resisting lacquers, which withstand the operations involved in forming and sealing cans, are available, but it is generally found that a single coat is not sufficient for protection and may even increase the risk of perforation and hydrogen-swells. Double lacquering is generally practised and usually has the effect of checking the discoloration otherwise produced. According to Morris and Bryan the ideal method of double-lacquering would be to put one coat on the flat sheet and spray a second into the interior of the finished can so as to cover up scratches and blemishes caused during its formation. Even then there is the damage due to the final sealing, and double-lacquering on the flat sheet is the more usual practice.

A. L. Matthison (*Chem. and Ind.*, 1930, **49,** 474) directs attention to the necessity of removing grease or palm oil left on the surface of the can from the hot-dipping process, which otherwise prevents the perfect adhesion of lacquer to the plate. He states that complaints of lacquer shelling or flaking can usually be traced to this cause. Heating appears to be the most effective means of removing the palm oil.

Discoloration of the food may be caused either by tin or by iron. Fruits containing anthocyanin pigments develop a more or less violet tint in the presence of tin ; in other cases an opalescence or muddy appearance, due to oxides or basic salts of tin, may be apparent in the syrups. Certain products may blacken the inside of the can by forming tin sulphide.

Lacquering the inside of the can is the chief remedy for discoloration and is essential with coloured fruits, but is not always effective in combating the bleaching action of nascent hydrogen produced in the can. The best method of reducing this bleaching appears to be cold storage.

The iron may cause blackening of the contents of the can by combination with tannins and other similar substances present in foods, but a more serious form is the blackening due to ferrous sulphide formed by the action of sulphur compounds on the metal ; this occurs especially with lobsters, crabs, and shrimps.

Lead Coatings.

Coatings of lead have the advantage of conferring comparative immunity to attack by sulphuric and sulphurous acid fumes and have excellent mechanical properties for· material which has to be seriously deformed. Lead coatings are recognised to form an unusually good basis for paint.

Hot-dipping is not successful with pure lead, for the molten metal does not alloy with the surface of iron or copper. The result is that the immersed article is never properly wetted, and on removal from the bath a coherent and continuous film is not obtained. If great care is taken to clean iron sheet before immersion in the lead bath a coherent film can be obtained, but its lack of uniformity makes it undesirable. It is more usual to add another metal which alloys with both the base metal and lead, such as tin or antimony, or in some cases both of these metals. The metals may be added directly to the bath or the sheet may be given a preliminary coating of tin and then dipped in lead. Lead coatings are apt to show pinhole perforations, but in the case of sheet this defect can easily be removed by rolling.

Relatively pure lead coatings can be made on iron and steel by a process described by Baskerville (*J. Ind. Eng. Chem.*, 1920, **12**, 1522). The pickled material is immersed in a solution of antimony chloride, whereupon a film of antimony is precipitated on its surface. On immersion in a bath of molten lead the antimony film acts as a binder.

Lead-tin alloys or " terne-plate " are used on iron, particularly for roofing. The dipping process is similar to that described for tin. The composition of the coating varies considerably, but 75 per cent. of lead and 25 per cent. of tin is a representative ratio. The material is less bright in appearance than the pure tin coating, and has a characteristic crystal pattern analogous to the spangle of zinc coatings. It is more resistant towards many types of corrosion.

Aluminium.

From the point of view of resistance to atmospheric corrosion one would expect aluminium to form an admirable protective coating for iron. Aluminium also alloys very easily with iron and the essential condition for the hot-dipping process is therefore fulfilled. Nevertheless, in practice the results are disappointing, and the coating of iron with aluminium by hot-dipping is difficult and is successful only after careful preparation of the surface of the iron. Probably the difficulty is partly to be attributed to the oxide film which forms so readily on aluminium and partly to the large amount of iron-aluminium compound which is formed. Iron and aluminium are completely miscible in the molten state. The aluminium coating is more effective if a coating of tin is applied first. Hot-dipped aluminium coatings on iron are not generally used as such, but are employed in the calorising process described on page 257.

CHAPTER IX.

ELECTROPLATING.

In several respects electroplating has the advantage over other methods of producing metallic coatings. The course of electrolysis follows quite definite rules which are embodied in Faraday's Laws of Electrolysis, and the amount of metal deposited is proportional to the current density and to the time during which the current flows. By varying these factors it is possible to regulate the thickness of the deposit with exactitude even where the thinnest coating is to be given. From the practical point of view, an electroplating installation can be adapted with very slight changes to the deposition of any metal ordinarily desired, and small-scale or large-scale work are carried out with equal ease. As the base metal is not subjected to heating, the method has an added advantage in that the mechanical properties of the metal do not suffer. Iron and steel goods are sometimes rendered more brittle by the absorption of hydrogen produced at the cathode, but this effect can be rectified by subsequently heating at 105° C. for a short time, when most of the hydrogen is driven off.

Copper, nickel, zinc, and chromium plating by electro-deposition are important industries, whilst decorative silvering and gilding by this process has long been carried out. Most other metals used commercially can be deposited by electrolysis when required for special purposes, but aluminium is

an outstanding example of failure in this respect. Aluminium reacts with water too readily. So long as the process is conducted in aqueous solution it is natural that the metals which are more noble than hydrogen in the electrochemical series will be deposited with greater ease. The electro-deposition of zinc is made possible largely by the high overvoltage of hydrogen at a zinc surface.

The fundamental principles of electrolysis are described in text-books of electrochemistry, and it is not considered necessary to discuss them in detail here. The electroplating installation consists of a tank containing a solution of a salt of the metal to be deposited. The metal to be plated is made the cathode or negative pole, and the anode or positive pole is usually a piece of the same metal as that to be deposited. In that case the anode dissolves and an equal amount of metal is deposited on the cathode, so that, provided no side reactions occur, the composition of the solution does not change. As a rule, however, the efficiency of the electro-deposition process is less than 100 per cent. This means that at the cathode all the current is not used in the deposition of metal. Other cathodic reactions which may occur are the evolution of hydrogen, the formation of hydrides, the formation of basic salts or of salts in a lower state of oxidation. Any current used for processes other than the deposition of metal is wasted so far as the electroplating is concerned. For some purposes an anode of an insoluble, conducting material, such as graphite, may be used. In that case the electrolyte becomes more and more dilute as the electrolysis proceeds, and other anodic reactions, such as the evolution of oxygen, occur at the positive pole.

The Structure of the Deposits.

Although the cathodic deposition of metals is a simple process, in practice successful results are obtained only when certain conditions are carefully chosen, because the physical character of the deposit varies with the composition of the bath, the current density, the temperature, and other factors. A smooth, hard and compact deposit, which adheres firmly to the underlying metal, is aimed at and a considerable amount of research has been done on different electrolytic systems to define the conditions under which such deposits may be obtained. Under other conditions the metal may be deposited in the form of large crystals or tree-like growths at certain spots on the cathode, or it may be deposited fairly uniformly in a porous, spongy form, which is quite unsuitable. The spongy form is obtained particularly when the electrolyte is a neutral solution and when high current densities are used. The evolution of hydrogen at the cathode under these conditions causes the solution in the immediate vicinity to become rich in hydroxyl ions, which react with the metal salt to form the hydroxide of the metal. It seems that the spongy deposit is often due to the co-precipitation of hydroxide with the metal, producing a lack of cohesion between the particles. When the current density is high, metal ions may be discharged more quickly than they can be replaced by diffusion and part of the current is then used in discharging hydrogen ions, reducing thereby the efficiency of the electro-deposition process. By stirring the solution, which can be performed most satisfactorily by rotating the cathode, the metal ions are supplied to the cathode at a greater rate and a higher current density may be employed without a loss of current efficiency and generally with an improvement in the deposit. Excellent deposits,

entirely free from sponge, are usually obtained in the electrolysis of complex cyanide solutions, and various explanations of the fact have been suggested ; for example, the very low concentration of metal ions, which is always maintained by the dissociation of the complex cyanide ion, which acts as a reservoir, or by the metal being deposited through a secondary reaction between a discharged alkali-metal ion and a complex cyanide ion or undissociated molecule. It may be, however, that the explanation is to be sought in the solubility of the hydroxide of the metal in the cyanide solution.

One condition for a smooth, hard deposit is the production of finely grained metal. This condition requires the formation of a large number of nuclei and a slow rate of growth of the individual nuclei. The various addition agents which are added to plating baths probably act by affecting this condition. In some cases, small quantities of colloids are specially effective, probably because the material is deposited with the metal and " protects " it from grain growth by forming a sheath around the grains.

Apart from the use of addition agents, the current density employed has an important influence on the hardness of the deposit. A very low current density gives rise generally to a coarsely crystalline and relatively soft deposit, whilst with increase of current density up to a point the deposit becomes more finely grained and harder. Above a certain limiting current density, however, a rough deposit is obtained, although the limiting current density may be increased by rotating the cathode. A low temperature may be expected to favour a hard deposit, since it inhibits grain growth.

H. S. Rawdon and W. Blum (*Trans. Amer. Electrochem. Soc.*, 1923, 245) have suggested a simple mechanism of crystal

formation in electro-deposition, according to which the cathode discharge of metal ions and the formation of crystals are one and the same process and any given ion is discharged at the point at which the lowest discharge potential is required. A higher potential is required to discharge an ion in a position unrelated to those of previously discharged atoms than on an existing crystal, and similarly a higher potential is required to discharge an ion on a small crystal than on a large one. Typical structures of electrode deposits are classified into three groups ; those in which practically all of the initial nuclei continue to grow, those in which only a part of the initial nuclei continue to grow, and those in which none of the nuclei grow.

D. J. MacNaughtan (*J. Iron and Steel Inst.*, 1924, **109,** 409) has measured the Brinell hardness of iron, nickel, cobalt, and copper deposited electrolytically under various conditions. The conditions of deposition which within certain limits have been found to cause increase of hardness are : (1) lowering of temperature ; (2) increase of current density ; (3) decrease of metal-ion concentration ; (4) increase of hydrogen-ion concentration. The first three of these conditions coincide with the factors which, according to W. D. Bancroft (*Trans. Amer. Electrochem. Soc.*, 1904, **6,** 27) cause a decrease in the crystal size of deposits, and the fourth condition has been noted by Hughes (*Trans. Faraday Soc.*, 1922, **17,** 442) and by Thompson (*Trans. Amer. Electrochem. Soc.*, 1922, **41,** 33) to favour small crystal size. There is therefore a close parallelism between hardness of the deposit and the size of grain. By adjusting these various factors it is possible to control the hardness of deposits of the metals studied within fairly close limits. Macnaughtan also discusses other views of the high hardness of

certain deposits. Simultaneous deposition of hydrogen with the metal, forming a hard solid solution is believed not to account for the effect, since the amount of hydrogen retained in solid solution seems insufficient to account for the high hardness attainable. Deposition of the metal largely in the amorphous condition is also thought to be improbable, though here it must be remembered that a microcrystalline aggregate, where the crystals have different orientations, must contain a considerable amount of intercrystalline boundary material which is not spaced in a continuous lattice. Displacement of the atoms from their normal positions in the crystal space lattice by electrical forces acting on them whilst they are being deposited and resulting in a deformation similar to that produced by cold working, is not considered to be a reasonable explanation of the increase in hardness. It is admitted that deposition of hydrogen with the metal may be one of the factors interfering with crystal growth, thus reducing the size of the crystals.

Later measurements by D. J. MacNaughtan and A. W. Hothersall (*J. Electroplaters' and Depositors' Tech. Soc.*, 1930, 5, 63) have given the following Brinell hardness figures for normal deposits : nickel 155-420, chromium 500-900, silver 61-130, cobalt 270-311, copper 58-150, cadmium 12-53, iron 167-350, zinc 40-50, lead 3-5. In general, soft deposits are more coarsely crystalline than hard deposits of the same metal. Coarse crystals are almost invariably associated with a matt appearance, but the surface becomes smoother with increasing fineness of grain, eventually having a bright, lustrous appearance in the case of a very fine and irregularly oriented structure. Smooth, hard deposits of nickel, silver, chromium, copper, and cadmium are capable of being polished more readily than

the rougher and softer specimens. Ease of polishing may vary inversely as the softness of the deposit.

R. M. Bozorth (*Physical Rev.*, 1925, [ii], 26, 390) examined by the X-ray spectrographic method electro-deposited films of copper, zinc, and cadmium and found the crystals to be oriented at random, whilst those of iron, nickel, and cobalt were found to have special orientations. The orientation is ascribed to hydrogen being deposited with the metal. The metallic atoms take up positions farther apart than normally, but as successive layers are added the hydrogen diffuses from the innermost layers, leaving the metal in a state of stress.

P. K. Fröhlich, G. L. Clark, and R. A. Aborn (*Z. Elektrochem.*, 1926, 32, 295) have used the X-ray method to study the relation between crystal structure and the electrochemical conditions during deposition of lead from acetate, nitrate, perchlorate, fluoborate, and fluosilicate solutions. The minimum grain size is given by deposits from a perchlorate solution in the presence of excess of acid and gelatin. In contrast to the behaviour of iron, nickel, and other metals, lead shows an increased preferential orientation with increasing current density. The grain size increases with the thickness of the deposit and the preferential orientation is less in the outer than in the inner layers. Gelatin retards the crystal growth and hinders the even distribution of the metal over the whole surface of the electrode.

V. Kohlschütter (*ibid.*, 1927, 33, 272, 277, 290) has carried out a detailed investigation of the electrolytic crystallisation process. As in other crystallisation processes, the result is determined both by the rate of formation of nuclei and the rate of growth of existing nuclei, and these two factors may be altered in different senses by a change of conditions. In a

review of theories of the mechanism of the cathodic deposition of metals it is shown that numerous factors may operate in determining the nature of the deposits, the growth being affected not only by the forces of crystallisation, but also probably by forces in solution. The size of the individual crystals is determined by the relation between the rate of crystal growth and the rate of nucleus formation, which in turn depend on current density, concentration of electrolyte, and temperature.

That forces operating in solution do affect the structure of the deposit in addition to crystallisation forces is clear from a study of the effects of addition agents and is illustrated by a recent investigation of the cathodic separation forms of tin carried out by F. Foerster and H. Deckert (*Z. Elektrochem.*, 1930, **36,** 901). They examined the influence of crude *m*-cresol-sulphonic acid in determining the form of tin deposited during the electrolysis of sulphuric acid solutions of stannous sulphate and found the effects to be due to the adsorption of a resin which is present to the extent of about 0·4 per cent. With small adsorption there is a tendency to the formation of needle-like aggregates or slimes, changing to white tin, and finally to a milky-white structureless deposit with maximum adsorption. High concentrations of *m*-cresol give a deposit similar to that formed in the presence of the resin, and is itself adsorbed at the cathode. The effect diminishes with rising temperature in accordance with the adsorption law, and other adsorbable materials, including other phenols, sulphates of aniline and pyridine, and gelatin, are also active. The observed adsorption effect is at a maximum at the points and edges of the crystals and at a minimum on the plane surfaces.

S. Kaneko (*J. Soc. Chem. Ind. Japan*, 1931, **34,** 94B) ascribes the effect of addition agents in electroplating baths to reduction

of surface tension of the solution, favouring the formation of a larger number of nuclei and to positive adsorption of the addition agent, producing a smaller grain size.

Uniformity and Adhesion of the Deposit.

Uniformity is one of the essential features required of any protective coating, but is attained in electroplating only by taking special precautions. In the simplest case, where two sheets of metal serving as electrodes are placed opposite and parallel to each other in the bath, the greater part of the deposit forms on the side of the cathode which faces the anode, and the back of the cathode may be almost free from deposit, except for a fringe round the edges. This is because the current density is not evenly distributed over the surface of an electrode, the current lines converging in the direction of the oppositely charged electrode. In addition, the current density tends to concentrate at the corners and edges of a rectangular electrode in a way similar to the well-known tendency of an electric charge to escape from a point.

Some experiments on the effects of this uneven distribution of current density over a rectangular electrode were made by E. S. Hedges (*J.C.S.*, 1929, 2710), who studied the anode mainly, but the general principle applies equally well to the cathode. Whenever film formation takes place at such an electrode the film first forms at the lowest part of the electrode and travels up the metal in the form of a **U** of diminishing concavity. This is not due to a concentration gradient in the solution, for the phenomenon occurs however vigorously the solution is stirred and is independent of the direction in which the liquid flows over the electrode. In experiments with the easily passivated metals some curious effects were observed through

this behaviour.   Anodes of iron were often found to be passive on the inside (*i.e.* the side facing the cathode) and active on the outside, where no oxygen was evolved ;   or, at somewhat higher current densities, the lower portion of the outside of the electrode became passive, leaving the upper portion active, with the characteristic U-shaped boundary of separation.   In certain cases a small active area was left near the water-line, where rapid corrosion took place.   In other cases the main portion of the electrode remained active, whilst just the corners and edges of the electrode became passive.   Some striking effects were observed with anodes of cobalt, which readily become passive, with evolution of oxygen, in moderately concentrated solutions of sulphuric acid.   In 50 per cent. (by volume) sulphuric acid cobalt dissolves at low current densities as a pink, cobaltous ion, but at higher current densities it goes into solution as a green cobaltic compound.   It was frequently observed that the inside of the electrode was dissolving to give a green solution, whilst the outside dissolved simultaneously to form a red solution.   These effects illustrate the difficulty of obtaining an even distribution of current density and consequently uniformity of chemical effect, whether dissolution or deposition.

In practice, the uneven distribution is counteracted as far as possible by a proper spacing of the anodes with respect to the articles undergoing plating, whilst if the conditions permit continuous movement of the cathodes the uniformity of the deposit is much increased.   Another difficulty in practice is that the articles are as a rule irregular in shape and that parts in high relief, being nearer to the anodes, receive a heavier deposit.   An unevenness on the surface becomes exaggerated. A serious matter is that recesses in the article may escape with

only a very thin coating, and in this respect solutions of different salts of the same metal differ considerably. This behaviour of solutions is termed their " throwing power." The complex cyanide solutions are characterised by a high throwing power, whilst chromium is particularly poor in this respect.

In order to secure an adherent deposit, careful cleaning of the base metal is essential, but there are other factors, all of which are not understood. Electro-deposited metal clings to the rougher parts of the base more firmly than to smooth portions and as a rule adheres to soft metals better than to hard metals. There is, on the whole, better adherence when the two metals alloy readily than when they do not, but metallographic examination fails to reveal a definite alloy layer analogous to that found after hot-dipping.

Electro-deposits of Zinc.

The position of zinc in the electrochemical series of metals would suggest that it cannot be deposited from aqueous solutions with a satisfactory current efficiency, a large part of the current being used in the liberation of hydrogen. However, hydrogen has an exceptionally high overvoltage at a zinc electrode and hence its evolution is not easily brought about. In practice, the electro-deposition of zinc is an efficient process, both from the acid sulphate solution and from solutions of zinc potassium cyanide. Both of these solutions are used in zinc electroplating establishments. The cyanide bath has the advantage of a greater throwing power and is therefore especially suitable for the plating of threaded articles or those having deeply recessed parts. The deposit produced from such a solution is more uniform and of finer texture than that obtained from an acidified zinc sulphate bath. The deposits from the

sulphate bath are more finely grained in the presence of various addition agents. In the coating of iron goods the cyanide bath has a distinct advantage in that the solution does not attack the iron.

Small articles, such as nuts and bolts, screws, washers, etc., are usually coated by the " barrel " method. The articles are placed in a perforated barrel, made of non-conducting material, which is immersed in the electrolyte solution. The articles form the cathode of the cell and are in contact with flexible metallic conductors on the inside of the cell. The anodes are rods of cast zinc, which are hung in the solution outside the barrel so as to encircle it. The cathodic barrel is supported horizontally in the solution and during the electrolysis is rotated about its longitudinal axis so that the articles tumble about and continually expose new surfaces to be plated. In this way an even deposit is ensured.

The other principal method in use may be called the " conveyor " method. The articles are hung on a chain conveyor, which is moved through the solution and passes between the anodes. The conveyor and the suspended articles constitute the cathode of the cell and the thickness of the coating received depends on the speed of the chain, or the length of time during which the articles remain in the bath. This method has the advantages of minimising the handling of the articles. After attaching them to the conveyor, they may be passed first through cleaning and washing tanks, then through the plating bath, and finally through washing tanks. The coating of wire, wire-netting, etc., is also made a continuous process, the wire passing through pickling and washing tanks, the plating and final washing tanks in turn.

Electro-deposited zinc coatings are simpler in structure than

those obtained by hot-dipping, there being no appreciable amount of alloy-layer present. Metallographically, it is as a rule not possible to demonstrate the existence of an alloy-layer at the junction of the base metal and coating, but there are reasons for believing that in many cases such an intermediate layer is formed, although it may be only a few molecules thick, and in certain instances its existence is indicated by X-ray spectrographic examination. The microstructure of the deposit varies between wide limits in general accordance with the rules, already described, relating to the regulation of crystal size. Chemically, the deposit is much purer than the hot-dipped coating. The average composition is 99·85 to 99·90 per cent. of zinc, with metallic and other inclusions depending on the nature of the anodes and of any addition agents. Small quantities of hydrogen are generally occluded. The mechanical properties of electro-deposited zinc are good and the coatings withstand severe bending particularly well. This is due in no small measure to the absence of an appreciable alloy-layer. The adherence of the coating to the base metal also appears to be greater for electrolytic than for other coatings.

Against corrosion, the uniformity and chemical purity of the electroplated coating ensures good protection, but this method is generally used for articles requiring a thinner coating. For withstanding severe corrosion the thicker coating obtained by hot-dipping is more usually applied. Electroplated zinc coatings containing about 2 per cent. of mercury have been reported by C. J. Wernlund (*Trans. Amer. Electrochem. Soc.*, 1924, **45**, 273) to be more resistant to corrosion than coatings of pure zinc.

Electro-deposited zinc has been applied successfully to copper, brass, and other industrial metals and alloys ; in parts

consisting of different metals the contact effect of dissimilar metals has frequently been avoided successfully by a plating of zinc.

Electro-deposits of Copper.

The protection offered to a metal such as iron by copper is quite different from that afforded by zinc. The polarity of the couple is reversed, for when copper and iron in contact are placed in a solution of an electrolyte the copper becomes the cathode and iron becomes the anode and dissolves. So long as iron is completely covered at every point by copper it is as immune from corrosion as copper itself, but if a break appears in the coating, with exposure of the iron, very severe corrosion of the iron is likely to occur at that point. Coatings of copper are not much used as a protective agent against corrosion, but are used for other purposes and merit a brief description here. The coatings do not have a very pleasing appearance and are not able to retain a high polish.

The plating solutions in common use are either copper sulphate acidified with sulphuric acid or a solution of the double cyanide of copper and potassium. The latter is used for plating iron, because the spongy deposit of copper which forms when iron is immersed in a solution of copper sulphate prevents the adherence of the electro-deposited film.

Copper films made by cathodic deposition are very firmly adherent to the base metal, and a great deal of attention has been paid to their structure (O. Faust, *Z. anorg. Chem.*, 1912, **78,** 201; A. Sieverts and W. Wippelmann, *ibid.*, 1915, **91,** 1; H. S. Rawdon, *Trans. Amer. Electrochem. Soc.*, 1916, **30,** 159). They usually consist of columnar crystals arranged perpendicularly to the surface of deposition. As usual, deposits from the double

cyanide solution are very finely grained. There is some indication that the copper is in a state similar to that of cold-worked metal, the state of strain being relieved by subsequent annealing.

The electro-deposition of films of copper on steel finds an important application in protecting portions of steel parts during case-hardening. It is often necessary to ensure that portions of the steel remain soft so that after the treatment such parts may be machined. Copper proves to be the most useful metal for preventing the access of carbon monoxide to the steel and the portions of the steel which are required to remain soft are therefore electroplated with copper before the treatment.

Electro-deposits of Brass.

By the use of complex cyanide solutions of both copper and zinc in potassium cyanide the two metals may be deposited simultaneously with ease, although this is not possible with solutions of the simple salts of these metals because of the great difference in the potentials of the metals. The deposit formed is a true alloy and not merely a mechanical mixture of crystals of copper and zinc, as can be determined by X-ray examination.

Brass deposits are made on iron and steel by this method mainly for the sake of appearance. The coatings applied are usually very thin and very soon break down under outdoor conditions of service. In ordinary domestic use they afford a certain amount of protection in a dry climate and give a pleasing appearance.

Electro-deposits of Nickel.

Nickel plating has become an extensive industry and is especially used on brass and on iron and steel. Nickel is

cathodic with respect to iron, and any discontinuities of the film soon show signs of rusting. As applied commercially, the average thickness of the film in the past has been only about 0·0003 in., and parts subject to wear or rubbing are bound to expose the underlying metal in time. It is generally conceded that a thicker coating is desirable. The smoothness and hardness of the deposit, its ability to take a high polish, its resistance to atmospheric corrosive influences, and the ease with which the surface tarnish can be removed, have accorded to nickel a very favoured place as a protective metallic film.

The deposits are usually made from a slightly acid solution of nickel sulphate p_H 5·5-6·5 and may be made directly on steel, but it is often thought desirable to give a preliminary thin coating of copper. Sometimes three layers are deposited in the order nickel, copper, nickel, especially when the material is intended for exposure to severe weather conditions.

Commercial coatings of nickel usually contain some iron derived from the impure nickel anodes. According to M. R. Thompson (*Trans. Amer. Electrochem. Soc.*, 1923, 44, 359) the presence of a small amount of iron produces a whiter, denser, and more finely-grained deposit than is obtained with pure nickel. There is, however, the danger of inclusion of particles of basic ferric salts, which give rise to a certain degree of porosity.

The plating of irregularly-shaped articles has made an investigation of " throwing power " essential. Experiments with copper solutions by W. Blum and H. E. Haring (*Trans. Amer. Electrochem. Soc.*, 1923, 44, 313) showed that the property was mainly determined by (1) the rate of change of cathode potential with current density ; (2) the conductivity of the solution ; (3) the cathode efficiency at different current densities,

whilst Haring (*ibid.*, 1924, **46**, 107) established for nickel deposition that any conditions which decrease the ratio of nickel ions to hydrogen ions in the cathode film decrease the throwing power.   The throwing power of moderately buffered solutions, such as those of nickel sulphate and boric acid, or nickel ammonium sulphate, is better than that of highly buffered solutions, such as those containing nickel sulphate, boric acid, and a fluoride.   A high concentration of nickel salt and the presence of a soluble chloride favour a good throwing power.

To ensure good protection the film of nickel must be perfectly continuous.   O. P. Watts and P. L. Deverter (*Trans. Amer. Electrochem. Soc.*, 1916, **30**, 145) showed that the most common cause of rusting of nickel-plated steel articles was due to the plating being perforated by small pores, which gave direct access to the underlying metal.   C. T. Thomas and W. Blum (*ibid.*, 1925, **48**, 69 ; 1927, **52**, 271) in a series of more extended investigations confirmed this result and showed the superior effect of an initial layer of copper in combating the porous effect.   Another outcome of these researches was to establish the fact that the degree of porosity of the deposits is decreased by increasing the thickness of the nickel layer. These investigations have encouraged the specification of a minimum thickness of 0·001 in. of nickel, and the production of composite coatings of nickel and copper.

The microstructure of electro-deposited nickel is characterised by smallness of grain-size, and in other respects varies with the conditions in the way described for other metallic films obtained electrolytically.   The hardness is particularly variable with these factors, the Brinell number varying between 180 and 240.   Slight reference has already been made to the condition of strain under which some metals are deposited,

but in the case of nickel this behaviour becomes a fact of great importance. Nickel coatings are frequently stressed internally in tension, and if a break once appears the coating may peel off in the form of rolls. The phenomenon is readily demonstrated by depositing nickel on one side of a cathode of platinum foil, when it is found that the foil becomes strongly bent, the nickel being on the concave side. An investigation of the phenomenon was made by V. Kohlschütter and H. Schödl (*Helv. Chim. Acta*, 1922, 5, 490, 593) in order to determine the relation existing between the microstructure of the deposits and the contraction, which was found to depend on the deposition potential. It was concluded that, when deposits showing a high contraction are formed, deposition takes place at first in a thin skin of hydrogen. When there is free evolution of hydrogen at the cathode the contraction is slight, the surface of the deposit has a bright and metallic appearance, but appears scaly under the microscope. When the evolution of hydrogen is small the deposit shows a greater contraction and has a brown appearance. The inner structures of the different deposits are practically identical when examined microscopically. The size of the particles is from $1\cdot4$ to $2\cdot2$ $\times$ 10^{-4} cm., and the conclusion was reached that the contraction is purely a surface phenomenon, due to the aggregation of particles, originally deposited in a highly disperse form, into particles of larger size. Larger particles generally appeared when an alternating current was superimposed on the ordinary direct current. Deposits obtained with a direct current alone were brittle, whilst those obtained with a superimposed alternating current were soft, but there appeared to be no relation between brittleness and the contraction phenomenon. The brittleness is probably due to the presence of hydrogen in

the metal. The superimposition of an alternating current causes a lowering of the cathode potential more or less parallel with the lessening of the contraction effect in the deposit.

D. J. MacNaughtan and R. A. F. Hammond (*Trans. Faraday Soc.*, 1930, **26,** 481) report that the presence of chromic acid in the nickel solution increases considerably the stress in the deposit, which in consequence readily peels off the base. This addition has less effect when the base metal is copper than when it is nickel or steel.

The nickel plating of aluminium and some of its alloys has become important in the manufacture of aeroplane parts which have to be soldered. The nickel can be soldered successfully, but the soldering of aluminium generally is apt to fail in the presence of moisture. The nickel coating shows a decided tendency to peel from an aluminium base, and according to E. Tassilly (*Bull. Soc. Chim.*, 1922, **31,** 973) the preliminary cleaning of the aluminium is all-important. All the successful methods have the effect of roughening the surface, and the nickel seems to adhere more tenaciously to the roughened surface.

The behaviour of sheet steel nickel-plated under various conditions towards different corrosion tests has been investigated by C. T. Thomas and W. Blum (*Trans. Amer. Electrochem. Soc.*, 1925, **48,** 69; 1927, **52,** 271). It was concluded that all nickel coatings are porous, and the only practicable method of reducing the porosity and increasing the protective value of the nickel is by the use of relatively thick coatings (not less than 0·001 in.). Nickel deposits with a high iron-content turn yellow and permit excessive corrosion of the underlying steel. Deposits which contain a substantial layer of copper, applied either prior to the nickel coating or between two layers

of nickel, furnish far better protection against atmospheric corrosion than deposits of pure nickel of equal thickness.

Electro-deposits of Chromium.

The protection of metals by the electro-deposition of a film of chromium has become a commercial success during recent years and has attained very great popularity. The solution generally used contains chromic acid and a little chromium sulphate, and the anodes are of the insoluble type, such as lead, which is not attacked by this solution except to form a film. Adherent coatings can readily be made on iron and steel, brass, copper, nickel, and cobalt.

The special properties of the film are not only its ability to take a high polish and to retain it even under severe conditions of corrosion, but also its hardness, which enables the surface to withstand abrasion to an exceptional degree. Chromium readily becomes passive in the air, and the passivity produced is more durable than that of iron. The protection afforded is mainly due to this phenomenon. A drawback of chromium plating is that the electro-deposit is rather porous and the coating is apt to fail unless it is fairly thick. It is more usual, therefore, first to give a coating of nickel or copper, or both, and finally to apply a thin film of chromium. This ensures the highly polished finish, which is so admirable a feature of chromium-plated articles, eliminates the surface tarnish which is gradually developed on other platings, and affords excellent protection from corrosion to the base metal. When abrasion has to be guarded against, a thicker deposit is given.

The hardness of the deposit renders it suitable for plating printing plates, increasing the length of service of the plates

without sacrificing any detail of the engraving. Similarly, dies may with advantage be electroplated with chromium, not only because the life of the die is thereby lengthened, but because the chromium surface is free from scratches, and material drawn through such dies acquires a very smooth surface.

Chromium-plating is excellent for service at high temperatures, and has been used in the glass and ceramics industries and for other apparatus which is normally exposed to elevated temperatures. Apart from the resistance of chromium to ordinary atmospheric corrosion, it is particularly resistant in comparison with most other metals to attack by sulphur and sulphur compounds. Chromium-plating is finding, and will continue to find, increasing application in chemical plant where sulphurous vapours are involved, such as the vulcanisation of india-rubber and in the coal-gas industry.

The high reflecting power of chromium, combined with its resistance to surface tarnish, has resulted in its use for reflectors in motor-car headlights and for other similar purposes.

The conditions and factors controlling the electro-deposition of chromium from solutions of chromic acid have been much studied in recent years. V. Schischkin and H. Gernet (*Z. Electrochem.*, 1928, **34**, 57) have examined the deposition of chromium from aqueous solutions of chromic acid containing small quantities of sulphates. At constant current density at low temperatures the deposit is brown and accompanied with oxide. With rise of temperature deposits of dull appearance are obtained and the current efficiency falls. Further rise of temperature produces a lustrous deposit, although at still higher temperatures a dull matt surface is obtained. Microscopical examination showed that the lustrous deposit is covered

with minute fissures and contains occasional cavities. The duller deposits obtained at lower temperatures or higher current density exhibit an irregular, granular structure, whilst a crystalline structure could not be recognised in the matt deposits obtained at higher temperatures. Rotation of the cathode, dilution of the chromic acid solution, and increase in the concentration of sulphate favour the formation of the lustrous deposit.

In practice the bright deposit is aimed at, although the matt deposit is capable of taking a high polish when satisfactory methods are used.

Some detailed investigations have been made by E. Müller and his pupils (*ibid.*, 1926, **32,** 399 ; 1929, **35,** 84, 222 ; 1930, **36,** 2). A study of the current density-potential curves in 30 per cent. solutions of chromium trioxide indicated that a film of chromium sesquioxide is formed at the cathode at potentials not exceeding $+$ o·3 volt. This diaphragm hinders the access of chromium ions, but not of hydrogen ions. The diaphragm becomes permeable at about $-$ o·7 volt and partial reduction of sexavalent to tervalent chromic ions begins. At still more negative potentials (about $-$ 1·1 volt) deposition of metallic chromium occurs and the diaphragm disappears. In the presence of foreign anions the diaphragm of chromium sesquioxide is mechanically imperfect and may be swept away by the disengagement of hydrogen, and this is considered to be the reason for the bright, coherent form of the deposit which is obtained in the presence of sulphates. Similar results are obtained if sulphate-free chromic acid containing tervalent chromium is used.

Further experiments demonstrated that pure chromic acid cannot be reduced electrolytically, but may be reduced

to the metal in the presence of sulphate ions. The smallest polarisation of a bright cathode is sufficient to cause the formation of a porous, invisible diaphragm covering the surface of the cathode. The diaphragm is composed of basic chromium chromate oriented in such a way that the basic part faces the cathode and the acid radical is on the outside. The film hinders the passage of chromic acid up to the electrode. When the cathodic polarisation is increased hydrogen ions become able to pass through the pores, but unless the associated anion is able to follow, in which case acid is formed within the diaphragm, the diaphragm will remain intact. Consequently, for anions of large diameter, such as chromate, chlorate, phosphate, etc., a very high cathodic potential is necessary in order to penetrate the film, and this accounts satisfactorily for the fact that pure chromic acid is not reduced. On the addition of sodium salts having smaller anions (fluoride, chloride, sulphate, etc.) the diaphragm is more readily penetrated and dissolves, the cathode potential becomes smaller than the hydrogen potential and an appreciable reduction of chromic acid ensues. Electrodes with rough surfaces caused greater reduction of chromic acid, apparently through the discontinuous nature of the film.

E. M. Baker and A. M. Rente (*Trans. Amer. Electrochem. Soc.*, 1928, 54, 337) state that at 45° C. chromium baths will give deposits having progressively lower minimum porosity as the concentration of the bath is increased. A bath containing 2·5 *M*-chromic acid gives least porous deposits at 55° C., the optimal thickness of the deposit being about 9×10^{-4} mm. As the temperature or concentration of the plating solution is increased, it becomes necessary to increase the thickness of the deposit to get the minimum porosity obtainable at that

temperature or concentration. Porosity is attributed to the contraction of the film after deposition. When the chromium film is thin, it will disintegrate into tiny pieces on contraction.

According to an investigation by H. L. Farber and W. Blum (*U.S. Bur. Stand. J. Research*, 1930, **4**, 27 ; Research Paper No. 131), there is little hope of radically improving the " throwing power " of the chromium-plating process. Quantitative measurements of the throwing power are given by the ratio of the weights of metal deposited on two cathodes, one of which is twice as far from a gauze anode as the other. If this ratio is greater than 2 : 1 the throwing power is negative. The best throwing power obtained was — 13 per cent. The conditions found to yield the best throwing power were (1) high temperature (55° C.), (2) high current density (35 amp./dm.²) ; (3) low concentration of chromic acid (150-250 gram per litre) and low content of sulphate ($CrO_3/SO_4 = 200$). These conditions usually require a potential of over 6 volts.

Electro-deposits of Tin.

For most purposes hot-dipping proves to be the most satisfactory way of applying tin coatings, but many small articles are coated with tin by an electrolytic process. Solutions of both stannous chloride and sodium stannite are used for the purpose, but a colloidal addition-agent appears to be a necessity in order to obtain a compact coating. Under ordinary conditions tree-like growths form very readily at the cathode. The electrolytic coatings have generally a very dull appearance and are afterwards polished.

Electro-deposits of Lead.

A special feature of lead coatings is their resistance to fumes of sulphurous and sulphuric acids, and they find applica-

tion in the lining of flues and in other situations, which are exposed to special corrosive influences. For such severe work the coatings are made thicker than usual (generally more than 0·003 in.).

Lead has a very marked tendency to be deposited on the cathode in the form of "trees" and moss-like growths, especially from solutions of the simpler salts. The baths used in commercial practice are solutions of the fluosilicate, fluoborate, and perchlorate of lead, with the addition of glue or other colloidal substance to aid in the deposition of a dense coating. The properties of the coating may afterwards be improved by slightly working the surface.

Electro-deposits of Cadmium.

Commercial cadmium coatings are always made by electrolysis, a solution of the double cyanide of cadmium and sodium being used, but have not found a very wide application. The appearance of the deposit is better than that of zinc, as it is capable of taking a good polish. As with zinc, the protection afforded by cadmium to iron is of the electrochemical type, the cadmium becoming the anode and corroding preferentially. As cadmium is closer than zinc to iron in electropotential the local current set up during corrosion of cadmium coated iron is less, and there is less wear on the cadmium; on the other hand, the same condition entails that the protection due to the cadmium extends over a smaller area of exposed iron. The corrosion-resisting properties of cadmium deposits on steel are said to be improved by heating at 200° to 300° C. The deposit assumes a yellow colour after heating, and the oxide film produced probably adds materially to the resistance to corrosion. Coatings of cadmium are often applied as a preliminary to nickel-plating.

Of recent years cadmium coatings have come into more general use than formerly, and the increasing use has occasioned a certain amount of discussion regarding the relative advantages of cadmium and zinc for this purpose. C. L. Hippensteel and C. W. Borgmann (*Trans. Amer. Electrochem. Soc.*, 1930, **58**, 23) give experimental data for the rates of corrosion of electroplated zinc, zinc alloy, and cadmium protective coatings on steel in a severely industrial atmosphere. Zinc and zinc alloy coatings corroded at a slower rate than cadmium coatings, but the result appears to vary with the type of atmosphere. A review of the use of cadmium as a protection against corrosion, including a bibliography from 1849 to 1929, is given by Siemens (*Z. Elektrochem.*, 1930, **36**, 101). The relative values of cadmium and zinc have been discussed in some detail by S. Wernick (*J. Electroplaters' and Depositors' Tech. Soc.*, 1931, **6**, 129, and numerous papers in *Industrial Chemist*). The rate of sacrificial corrosion of cadmium is shown to be less and its durability correspondingly greater than in the case of zinc, but with porous coatings the intrinsic protection afforded by zinc is greater. This accounts for the variation of resistance to corrosion experienced in practice. A critical thickness of 0·0002 in. is required for resistance to corrosion, and the minimum thickness of deposit recommended for the prevention of rust is 0·0003 in. Cadmium-plating is considerably less reactive to most ordinary chemical reagents than is zinc plating.

Electro-deposits of Gold and Silver.

The production of films of gold and silver constitutes the earliest form of the application of metallic films, and ornamentation was the main object. Gilding was practised in

Egypt as early as 3000 B.C., although the process consisted merely of the application of gold hammered into foil. Ornamentation is still the main object of gilding and silvering, although in a few instances, such as the gold-plating of standard weights and the silver lining of certain laboratory apparatus, prevention of corrosion is the reason.

Commercial electroplating of silver dates from about 1840, and in both silvering and gilding the complex cyanide solution is used. The addition of a little carbon bisulphide to the silver solution results in the formation of a bright deposit. An average thickness deposited on articles of tableware is 0·0008 in. Silver coatings suffer from the disadvantage that they are readily tarnished by compounds containing sulphur. The recent changes in the economic position of silver may eventually have far-reaching effects in its application to chemical plant. Silver is attractive for chemical plant because it does not oxidise, resists various chemical acids, and has excellent mechanical properties ; in time the silver-plating of baser metals may attain considerable economic importance apart from serving as a means of ornamentation. Already silver is used in plant for the condensation of acetic acid, in food-stuff industries, in the manufacture of acetate rayon silk, and in several smaller industries.

Gilding has little interest except from the decorative point of view. By the addition of other metals coloured deposits of alloys are produced. Thus, the addition of copper produces a red gold, silver gives a green gold, and white gold is obtained by adding nickel to the solution.

Electro-deposited Metallic Films on Aluminium.

With the development of aircraft the protection of aluminium and the light aluminium alloys has acquired a special

significance. Not only is resistance to atmospheric corrosion necessary, especially under humid conditions, but resistance to sea-water is equally desirable. The problem is complicated by the fact that lightness of the resultant material is a controlling factor and, further, the parts may be subject to considerable stress.

The protection of aluminium by anodic oxidation has been discussed on page 183, and the coating thus produced has the advantage of lightness, but advances have also been made in recent years in the electro-deposition of other metals on an aluminium surface.

Some of the results obtained at the Royal Aircraft Establishment, Farnborough, are summarised in a paper by H. Sutton and A. J. Sidery (*J. Inst. Metals*, 1927, **38,** 241). Preliminary experiments showed that the preparation of the aluminium surface is of importance, and sand-blasting appeared to be the most satisfactory method.

Zinc coatings can be applied satisfactorily from a cyanide bath containing in 1 litre of water 75·0 grams of zinc cyanide, 37·4 grams of sodium cyanide, and 25·0 grams of sodium hydroxide, or from a sulphate bath containing 200 grams of hydrated zinc sulphate and 0·1 gram of β-naphthol per litre. The acidity of the sulphate bath is important, and the best results are obtained over the range p_H 3·5 to 4·5. The cyanide bath has the advantage of a greater throwing power. Zinc-plated samples of aluminium and Duralumin showed little evidence of corrosion of the aluminium after immersing in sea-water for twelve months, although the coating applied was only 0·0005 in. thick.

Cadmium coatings can be deposited from a solution originally recommended by Brunner (" Elektrolytische Abscheidung

der Metalle aus den Cyanidelösungen," Dresden, 1907), which consists of 8·2 grams of cadmium cyanide and 29·8 grams of potassium cyanide in 1 litre of water. At the ordinary temperature and using a current density of 4 to 12 amps. per sq. ft. of cathode, with anodes of high-grade commercial cadmium, the bath has good plating properties and a high throwing power. The deposits give good protection to aluminium alloys, but are relatively poor on pure aluminium, especially under marine conditions.

Nickel coatings on aluminium have been mentioned on page 234. Sutton and Sidery found that samples of nickel-plated aluminium having deposits of approximately 0·0005 in. showed serious corrosion at numerous points over the surface at a very early stage when submitted to sea-water immersion and spray tests. Severe local pitting of the character associated with the formation of local electrolytic cells was observed, and it seems that deposits of this thickness are porous. A minimum thickness of 0·001 in. is recommended for the nickel film from the point of view of corrosion protection, but such a coating is too heavy for aircraft, although doubtless satisfactory for other purposes.

H. K. Work (*Trans. Amer. Electrochem. Soc.*, 1928, **53**, 361) states that electroplates of most metals on smooth surfaces of aluminium are of doubtful value unless heat-treated. Plating on a roughened surface is recommended. Ballay (*Compt. rend.*, 1930, **190**, 305) gives a method for obtaining adherent electro-deposits on polished aluminium without sand-blasting or otherwise roughening the surface. An adherent deposit of iron is first obtained from a hot solution containing 6 to 22 grams of ferric chloride per litre and 0·1 to 0·7 *N*-hydrochloric acid. This layer may be nickelled with an indestructible

coat, and the nickel deposits will take a copper or chromium deposit well. J. Cournot and J. Bary (*Rev. Mét.*, 1929, **26,** 312) found that electro-deposits of chromium, nickel, and cadmium gave promising protection to aluminium against sea-water, but had not a satisfactory protective effect on magnesium. J. Cournot and E. Perot (*ibid.*, 318, 367) obtained good results from the cementation of these electro-deposits on aluminium by heating in sand, especially with complex deposits, such as copper-nickel and copper-chromium.

CHAPTER X.

SPRAYED METAL FILMS.

THE application of thin metallic films by spraying the molten metal on to the object has developed from the first experiments of M. V. Schoop (*Rev. Mét.*, 1910, **7,** 585). Briefly, the method consists in breaking up a thin stream of molten metal into a finely divided state by means of a strong blast of air or other gas and projecting the particles produced thereby on to the surface to be coated.

The apparatus consists of a " pistol " of light weight, which can be held in the hand so as to direct the stream of metal at will. In its original form the apparatus was unwieldy and was not portable. The pistol apparatus is a very great advance in technique, because structures such as bridges, parts of ships, etc., may be sprayed *in situ*, and difficultly accessible parts may also be coated. The metal is fed to the sprayer in the form of a thin wire at a constant rate so that it is replenished as fast as it is melted and sprayed. The thickness of wire depends on the metal, thicker wires being permissible in the case of metals of lower melting-point. For tin and lead the diameter is commonly 1·5 mm., for aluminium and zinc 1·0 mm., and for bronze, brass, and nickel 0·8 mm.

In the usual form of gas-fired pistol the wire to be sprayed is led through a central tube in the nozzle of the pistol, which consists in all of three concentric tubes. Through the tube

surrounding the central tube is passed the gaseous mixture of hydrogen or acetylene and oxygen or air, which burns at the orifice and melts the protruding part of the wire. The outer surrounding tube is a channel for compressed air or other gas which " atomises " and projects the metal as it is melted. The gas mixture used for heating depends on the melting-point of the metal ; for zinc, lead, and tin a mixture of coal-gas and air suffices.

An electric pistol has also been devised, in which the metal is melted in the electric arc formed between two wires of the metal to be sprayed, and the molten metal is projected by means of an air-blast.

For the spraying of zinc an older method is still in use to some extent. Zinc dust is the starting material for this process, as it is cheaply obtained as a by-product from zinc smelters. The zinc dust is forced through the flame of the blow-pipe, and the final result is similar to that of feeding with a metal wire.

In a recent improvement of the apparatus the fine metal dust is forced by compressed carbon dioxide at 7 to 8 atmospheres through openings into a chamber heated by an oxy-acetylene flame. The metal is thus heated indirectly with neutral gases at a high temperature, does not come into contact with atmospheric oxygen or directly with the flames, and oxidation of the metal particles is prevented.

Applications.

The two great advantages of metal spraying over all other methods of applying metallic films are that the coating may be applied to the structure *in situ* and may be applied at any desired spot. Moreover, the film is applied to the finished

article, so that as a rule the mechanical properties of the deposit are not of great importance, as no further working or operations of fabrication have to be carried out. The thickness of the deposit is controllable between fairly narrow limits, and in this respect the process is second only to electroplating. The fact that the spray can be directed to any desired location means that particular care can be taken with objects of irregular shape to secure a uniform film, and it makes the process particularly suitable for " touching up " coatings which have been applied by other processes. For example, sherardised coatings (see p. 255) frequently show defects, which can very simply be covered up by application of the spray. If certain parts of the object are subject to extra wear they can be given a thicker coating without having to treat the material as a whole. Indeed, it is possible to apply a coating 1 mm. or more thick for the purpose of withstanding chemical attack, or a very thin film may be added for providing a suitable surface to hold a coat of paint.

Thorough cleaning of the surface to be coated is an important preliminary operation, and experience goes to show that sand-blasting is the best ; this has the effect of slightly roughening the surface and no doubt thereby supplies a better grip for the particles of metal. Probably the adherence of the metal is purely mechanical ; it is often improved by heating the object to about 250° C.

In large-scale structures, metal spraying is employed for the zinc coating of the towers for the overhead bearing of electric cables and for wireless stations, and also for bridges, the hulls of ships and other more or less fixed fabrics. In cases of this sort there is the added advantage that the coating may be renewed when necessary without dismantling the struc-

ture. On the smaller scale the applications are numerous, and the process is often used entirely for decorative purposes. In fact, metal spraying can be applied to articles of wood, clay products, paper, and other material. The process has been applied successfully to the protection of aluminium and the light aluminium alloys against atmospheric corrosion, a problem which is becoming of increasing importance with the development of aircraft, and which has not been solved to entire satisfaction by other methods of metal deposition. At the same time, it is possible to produce coatings of pure aluminium on other metals by use of the spraying pistol, and this object cannot be attained satisfactorily by other means. Such coatings are particularly useful in affording protection at high temperatures, for the surface of the aluminium itself acquires a resistant, protective film of oxide. Aluminium alloys very readily with other metals, and such coatings gradually deteriorate at elevated temperatures through the diffusion of the aluminium into the base metal, but a new coating can easily be applied when required. An interesting feature is the protection of Duralumin by spraying with pure aluminium, which offers resistance to salt water. Metal spraying is also an admirable method for the lead-coating of chemical plant. Another valuable feature is that two metals may be applied, either simultaneously, or in succession.

Structure of Sprayed Metal Films.

T. H. Turner and W. E. Ballard (*J. Inst. Metals*, 1924, **32**, 291) have made a microscopical study of the structure of sprayed metals on a glass surface, and the photomicrographs obtained remind one of the splashing of rain-drops against a window pane, each " splash " solidifying on impact. They

reached the conclusion that at the moment of impact the metal particles are either still molten or are very plastic. On the other hand, the fact that metal may be sprayed on to paper without any charring suggests that the particles are already cooled well below their melting-point, and that they are flattened into thin scales by the force of the impact. The spreading caused in this way increases very considerably the covering power of the metal and is an important factor affecting the coherence of the individual scales.

The mechanism of production of the film by the overlapping of the scales suggests the probability of a rather porous structure, and examination of the microstructure of the films by H. Arnold (*Z. anorg. Chem.*, 1917, **99,** 67) and by H. S. Rawdon (*Proc. Amer. Soc. Testing Materials*, 1918, **18,** Part 1, 216) indicates a laminated structure, whatever the metal used. It would seem, however, that the stratification is due largely to the oxidation of the surface of each particle of the metal, thus interfering with the perfect cohesion which might result were this condition absent. A certain amount of oxide is generally present in the film when it is applied with the aid of an air-blast, and when the metal particles are projected through the agency of a blast of some inert gas the laminated appearance is very much reduced.

The inclusion of oxide in the structure of the film in the way suggested leads to porosity, and this defect is generally present in films which have been sprayed with the aid of compressed air. It is asserted that in most cases moisture is able to creep in under the film. The porosity is reduced, however, by the use of an inert gas, and Turner and Ballard (*loc. cit.*) claim that even with the use of an air-blast under careful control it is possible to obtain quite impervious films

of lead, tin, and zinc. As a crucial test, they sprayed sticks of metallic sodium with lead and tin and the covered sticks were found not to react with water.

Some disagreement exists about the hardness of sprayed metal, some reporting an increased hardness and others the reverse. Probably the different methods of application and the different amounts of oxide-inclusions account for the discordance. The ductility and impact resistance of samples of metal built up entirely by spraying are low. The density is generally lower than that of cast metal, but this is partly attributable to the inclusion of oxide and to the presence of cavities filled with gas. The effect of oxide inclusions is made apparent by the fact that metal sprayed in the presence of an inert gas has a density approximately equal to that of the cast metal. The density can also be increased by polishing, a process which also diminishes the porosity, thus increasing the protective qualities of the film, and simultaneously improving the appearance of the finished article.

Metallographic examination has not succeeded in detecting the slightest evidence of the presence of an alloy-layer between the coating and the base metal, but the fact that the adherence of the film is better when applied to a heated base metal suggests that some such action does occur at the surface, even though the alloy-layer may be only of molecular dimensions.

A full account of the metal spraying process has been given by T. H. Turner and N. F. Budgeon (" Metal Spraying," 1926, Griffin & Co., London).

CHAPTER XI.

CEMENTATION.

A FURTHER means of protecting a metal from corrosion consists in alloying its surface with another metal by a process which is known as cementation. The process is in some ways analogous to hot-dipping; the coating metal is, however, not applied in the molten state, but in the form of powder, in which the base metal is heated. In brief, the articles are packed in the powdered coating metal and are heated at a temperature somewhat below the melting-point of the more fusible metal, when diffusion of the coating metal into the base takes place and an alloy-layer is formed.

As the temperature of cementation is below the melting-point of either constituent of the alloy the mechanism by which the alloying occurs is not clear and has given rise to considerable divergence of opinion. Much has been written about the diffusion of metals in the solid state, but whilst some believe that intimate contact of the two metals is sufficient to account for such diffusion, others ascribe an important rôle to the vapour pressure of the cementing metal at the temperature of the process. In practice it seems that intimate contact is necessary.

It was established a considerable time ago by W. Hallock (*Bull. U.S. Geol. Survey*, 1890, No. 60, 147) that fusion may take place at the points of contact of different metals if the temperature rises above the eutectic-point, even if it does not reach the melting-point of the most easily fusible metal present.

He succeeded in preparing a liquid globule of Wood's metal by heating, in the requisite proportions, fine filings of cadmium (m.p. 320°), tin (m.p. 232°), lead (m.p. 326°), and bismuth (m.p. 269°) at 100° C. Melting occurred at the contact of pieces of tin and lead when heated at 190° C. Hallock concluded that in general an alloy can be produced from its original constituents without considerable pressure when the temperature is above the melting-point of the alloy, even though it may be far below the melting-point of the most easily fusible constituent. This conclusion is confirmed by the work of C. Benedicks and R. Arpi (*Rev. Métal.*, 1907, **4**, 416). It is interesting to note that the principle does not hold only for metals, but may be observed also in geological formations ; L. Hawkes (*Min. Mag.*, 1929, **22**, 163) has described rocks that have suffered partial fusion, which has been restricted to the contacts of quartz and felspar grains, neither quartz nor felspar showing any signs of melting.

G. Sirovich and A. Cartoceti (*Gazzetta*, 1922, **52**, [ii], 233, 245) have studied the cementation of copper by means of ferromanganese and chromomanganese, and state that the first effect is the formation of a layer of alloy of a definite concentration, which is followed by the flow of the cementing metal into the interior of the base metal. They suggest that the alloy has a definite dissociation pressure at the temperature of cementation.

G. Grube and K. Schneider (*Z. anorg. Chem.*, 1927, **168**, 17) heated a bar of iron in contact with finely-divided tungsten for intervals varying between 15 and 72 hours at 1280°, 1330°, and 1400° C. and determined the extent of diffusion by analysis of successive layers, each 0·05 mm. thick, ground from the surface of the bar. Curves relating the percentage of tungsten

with the depth of penetration show a well-defined break, the depth at which the break occurs increasing with the duration and temperature of heating.

G. Grube and F. Lieberwirth (*ibid.*, 1930, **188**, 274) have studied the diffusion of molybdenum into iron by heating cylindrical rods of pure iron embedded in powdered molybdenum in a stream of hydrogen at temperatures from 1000° to 1300° C. At the latter temperature, after twenty-four hours' heating, the amount of molybdenum present at a depth of 1·5 mm. was 0·25 per cent. The coefficient of diffusion increases with the distance from the surface and attains an approximately constant value in the innermost layers examined. Homogeneous alloys were made by heating compressed mixtures of powdered molybdenum and iron for seventy-two hours at 1250°, and these were found to be resistant to the action of 0·1 *N*-hydrochloric or sulphuric acid, especially when the alloy contained about 5 per cent. of molybdenum. The protective action was lower in alloys of higher molybdenum content, in which metallographic examination revealed a heterogeneous structure.

Cementation processes are necessarily restricted to metals which are capable of forming an alloy with the base, and there are three processes of prime commercial importance. These are known respectively as " sherardising," " chromising," and " calorising," the applied metals being respectively zinc, chromium, and aluminium, whilst the base metal is almost always iron or steel. These methods will be discussed individually later.

The cementation process is particularly suitable for small articles, and the general procedure is to pack the articles with the cementing metal powder, sometimes with the addition of

a diluent, in a container, which is rotated about an axis in order to ensure uniform contact with the powder, through the articles tumbling about. The container is generally heated electrically. In some cases air is excluded and hydrogen substituted.

The coating produced is essentially an alloy, and in some respects can be regarded as analogous to the under alloy-layer produced by the hot-dipping process. Alloy layers are in general far more brittle than coatings of pure metal, and cementation is not therefore a good method for protecting articles which have to withstand deformation in service, or which have to undergo subsequent fabrication involving deformation.

Sherardising.

The cementation of iron with zinc was discovered quite accidentally. Some iron and steel samples were packed in zinc dust as a supposedly inert substance, and the effect produced was noted and developed into a commercial process by Sherard Cowper-Coles, after whom the process is named. Sherardising dates from 1910, although the cementation principle is of much older standing.

The type of coating obtained depends to a large extent on the duration of heating and on the temperature. For general purposes a temperature of 350° to 375° C. is usual, but higher temperatures are often used. Zinc melts at 419° C. The zinc dust used is a by-product of zinc smelting and contains about 85 to 90 per cent. of zinc and 5 to 8 per cent. of zinc oxide. The iron-content of the material is said to affect the coating. The fine dust tends to cake on heating and the caking becomes troublesome after repeated use, but the trouble is overcome in practice by the use of a mixture of 90 per cent. of used material with 10 per cent. of new dust.

Examination of the structure of the film shows that most of it is one layer having a fissured appearance, the outer part being rough, whilst on the inner side a thin layer of another alloy richer in iron is often found. The average iron-content of the alloy constituting sherardised coatings is 8 to 10 per cent., and according to O. W. Storey (*Met. Chem. Eng.*, 1916, **14**, 683) the main layer of the coating has a composition which approaches closely to the composition $FeZn_{10}$ (7·8 per cent. of iron). When the temperature is higher or the duration of cementation is longer a second alloy-layer appears between the outer coating and the base metal, and it is probable that this consists of the compound $FeZn_3$. In cases where the two metals are capable of forming intermetallic compounds the composition of the alloy-layer does not vary continuously with the depth, but in quite definite steps, and photomicrographs of sections show that the alloy-layers have quite definite boundaries. An average sherardised coating has a thickness of about 0·0025 in. and corresponds to three hours heating at 375° C.

The iron-zinc alloys are anodic to iron and the protection afforded by the sherardised coating is of the electrochemical type, like that of pure zinc, but the difference of potential is less. During weathering, both the iron and zinc constituents of the alloy undergo oxidation and in films of low iron-content a dark grey or black film of the mixed oxides forms on the surface. This oxide film has protective properties and such sherardised materials are therefore resistant. When, however, the iron-content of the alloy rises to the neighbourhood of 15 per cent. the resistance of the coating to atmospheric corrosion is very low. In this case the product of oxidation is a red, loosely adherent powder, which offers no protection to the underlying metal. The use of a poor quality of zinc dust rich in iron leads to the mechanical inclusion of

particles of iron in the outer coating, and rusting then occurs readily on weathering.

Chromising.

Through the marked advances which have been made in recent years in the production of pure chromium-plating by electro-deposition the chromising process has not developed to the extent that it might have done. The process is in its essential features precisely similar to sherardising and is useful for the coating of iron or low-carbon steel, but is difficult with high-carbon steels. The articles are loosely packed in a drum with fifty-five parts of powdered chromium and forty-five parts of powdered aluminium oxide, which acts as a diluent. The temperature is high (1300° to 1400° C.) and oxygen and water vapour must be excluded, since they would react at the surface of the chromium, producing a highly resistant protective film of oxide, which would insulate the chromium particles from the base metal. An inert atmosphere, preferably of hydrogen, is essential. The best conditions have been investigated by F. C. Kelly (*Trans. Amer. Electrochem. Soc.*, 1923, **43**, 351). Ferrochromium powder may also be used.

Chromium and iron alloy very readily with each other, and examination of the microstructure of chromised coatings shows that the chromium is in solid solution in the iron. A chromised surface can readily be polished, and is not so hard as electroplated chromium surfaces. The chromised coatings are particularly resistant to attack by dilute nitric acid, but are not resistant to hydrochloric acid.

Calorising.

The cementation of a metal surface by means of aluminium is called calorising and is similar to the sherardising process.

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In the older method the articles are loosely packed in a drum which is partly filled with powdered aluminium and aluminium oxide together with a little ammonium chloride. Aluminium melts at 659° C., but the temperature used in calorising is higher than this, being about 900° to 950° C. for iron and steel and 700° to 800° C. for the coating of copper and brass. The aluminium oxide prevents the coalescence of the droplets of molten aluminium. An atmosphere of hydrogen is maintained.

At the present time it is more usual to perform the calorising process in two stages (compare p. 215), the metal first being hot-dipped in a bath of molten aluminium and subsequently heated, whereupon the aluminium diffuses into the base metal, and the final result is similar to that obtained by the ordinary, direct cementation process. The coating has a thickness of 0·001 to 0·004 in. when ready for use, but when employed at high temperatures the aluminium diffuses further into the underlying metal and the coating becomes thicker, but at the same time less useful, because the concentration of aluminium diminishes in proportion.

L. Guillet and V. Bernard (*Rev. Mét.*, 1914, **11**, 263) studied the diffusion of aluminium into iron at 635° C., and the resulting narrow zone of interaction after fifty hours' treatment was taken to consist of $FeAl_2$. E. D. Martin (*ibid.*, 1925, **22,** 139) introduced mild steel into molten aluminium at 850° C. for one hour. After removal, three zones could be distinguished : (*a*) aluminium containing a small amount of crystals of $FeAl_3$; (*b*) a solid solution of $FeAl_2$ in $FeAl_3$; (*c*) a thin layer of a solid solution of aluminium in iron. Beyond this was a layer of iron, the edges of which were rich in carbon, which is insoluble in alloys of aluminium and iron. N. W. Ageev and O. I. Vher (*J. Inst. Metals,* 1930, **44,** 83) find that

the process takes place in two stages : (*a*) dissolution of iron in liquid aluminium ; (*b*) diffusion of the alloy formed into solid iron. The rate of diffusion falls off rapidly as the time of treatment is prolonged.

Calorised metals are designed primarily for service at high temperatures, where the resistance to oxidation is high. The aluminium acquires a superficial film of oxide, which protects it from further attack. At temperatures not exceeding 900° C. the life of calorised iron is said to be almost unlimited, but as the temperature is raised still further the diffusion of aluminium away from the surface of the metal becomes a serious matter, for if the outer protective layer of aluminium oxide then becomes broken it cannot be repaired because the composition of the metallic surface no longer provides the requisite type of oxide film.

A further extremely useful feature of calorised coatings is their resistance to attack by sulphurous fumes, and this has led to the adoption of the process for the manufacture of retorts, condenser parts, etc., used in the oil-refining industry and to structures used in the coke industry.

Coatings resistant to high-temperature oxidising conditions can be applied to iron by spraying aluminium and even by the application of aluminium paint. When such products are heated, the aluminium readily diffuses into and alloys with the iron, giving a calorised coating, so that in the end such processes may be regarded as special modifications of the calorising process.

C. Commentz (*Korrosion und Metallschutz*, 1929, 5, 248) describes a process of " alumetising," which consists of spraying iron with a thin coating of aluminium and then heating to make the aluminium diffuse. The metal does not scale on heating below 1100° C. and is suitable for fire-bars in boilers.

CHAPTER XII.

MISCELLANEOUS PROTECTIVE METALLIC FILMS.

In the preceding four chapters the principal methods in use for the protection of metals by the application of other metallic films have been described. There remain several processes, some of them old but still having a limited application, which are employed in special circumstances.

A mechanical method suitable for coating sheet products consists of rolling an ingot of composite material, containing a core of the metal to be protected and an outer thick casing of another metal. When the composite ingot is rolled, the sheet obtained has a uniform coating of the protective metallic film, the thickness of which depends on the degree of reduction received in the working. Alternatively, the material may be drawn into wire. For the process to be successful it is essential that alloying of the two metals take place at their surface of separation, and in addition both metals must have the necessary rolling or drawing characteristics. The process is useful for the coating of soft-steel sheet with copper or nickel. Coatings made in this way are dense and compact, and generally superior to others in their freedom from perforation by minute holes.

Lead is very easily coated with tin by the simultaneous rolling of the two metals. Ordinary tin-foil is made by rolling a slab of cast tin down to the required thickness. For many purposes, however, pure tin-foil is not necessary and a foil made of lead and coated on each side with tin is used. This

is made by rolling a composite ingot obtained by casting tin round a bar of lead.

The old process for making Sheffield plate is another application. A slab of copper containing zinc and lead in solid solution was heated nearly to the melting-point of silver whilst in contact with a silver plate, and after removal from the furnace the product was rolled to the desired thickness. Gold-filled articles, such as watch cases, are made from gold-plated sheet, which is prepared by a similar process. The film of gold is about 0·003 in. thick.

In 1924 an English Patent was taken out for a process of mechanically covering aluminium with a heavy metal, such as copper, nickel, lead, etc. The process consisted of heating the aluminium to 300° to 350° C., spreading a layer of metal such as tin over its surface and then pressing on a thin, cleaned sheet of the heavy metal, using hydraulic pressure, and cooling under pressure. A mechanical process is used in the German Allautal and Duralplat, and the American Alclad alloys (*U.S. Nat. Advis. Committee Aeronautics*, Tech. Notes, No. 259, 1927), the alloys Lautal and Duralumin of high-tensile strength being plated by a pressure process with a coat of 99·95 per cent. aluminium. This gives the corrosion resistant properties of pure aluminium with the strength and hardness of the alloys. Thin sheet may be heat-treated without any undue diffusion of the alloying metal into the outer pure layer.

The tinning of copper is done on quite a large scale by hand. The copper sheet is heated and on to the heated surface are dropped scraps of tin and a small amount of ammonium chloride, which acts as a flux. A fairly uniform coating is obtained by rubbing with a wad of cotton waste.

The chemical deposition of a metal is sometimes utilised. The process is strictly an electro-deposition, but no external

current is applied, the materials used forming a short-circuited electrolytic cell. An iron wire immersed in copper sulphate solution acquires a film of copper, and simultaneously an equivalent amount of iron is dissolved. The deposit of copper is very spongy and is quite useless in its primary state, but if the wire is subsequently drawn through a die and reduced very considerably the copper film is made firmly adherent. The principal use of such a film is, however, for improving the appearance.

The principle of the short-circuited cell is also employed in the tin-plating of safety-pins, buckles, and other small articles of brass or steel. In this case a definite, separate anode is used, although no external current is applied. The articles are placed in contact with sheets of tin in an electrolyte, which consists of a hot solution of sodium chloride and potassium hydrogen tartrate. The tin becomes the anode of this cell and dissolves and is then precipitated on the articles of brass, which form the cathode. For tinning steel articles, ammonium alum is added to the solution and the conditions of the bath are varied slightly. The deposition of tin is limited by the fact that as soon as the surface of the brass article becomes covered with tin the electrolytic couple no longer exists and the process automatically comes to an end. The coating produced is therefore very thin and uniform. In brightness the film of tin exceeds that deposited by the ordinary electrolytic method.

An adherent, though extremely thin (some millionths of an inch) coating of gold is applied to cheap articles by immersing articles of copper or brass in a solution of a gold salt. Some copper, or copper and zinc, pass into solution and an equivalent amount of gold is reduced and forms on the surface of the article.

APPENDIX.

PAINTS, LACQUERS, ENAMELS, ETC.

AMONG other ways of excluding corrosive agents from the surface of metals by applying films of foreign material is the use of certain familiar greases and oils. These probably act in the main by excluding moisture. Numerous greases and oils are in use for this purpose, but special mention may be made of vaseline and lanoline. Experiments on the protection of brass by immersion in molten lanoline at 100° C. are described by W. H. J. Vernon (*Trans. Faraday Soc.*, 1927, **23**, 145). C. Jakeman (*Dept. Sci. Indust. Res. Eng. Res. Spec. Rep.*, No. 12, 1929, 1) states that acid-free lanoline is superior to petroleum grease for the protection of metals liable to corrosion. Solvent naphtha and white spirit proved to be the most suitable media for application. A. Wolf (*Trans. Faraday Soc.*, 1927, **23**, 193) states that the usual commercial procedure when using lanoline as a protective agent is to dip the article to be coated in a 10 per cent. solution of lanoline in a non-inflammable solvent such as trichloroethylene. This method has been used with great success to protect aeroplane engines from atmospheric corrosion during transport and storage. The direct application of greases to metals is generally a temporary measure, as such films are often undesirable in service.

A method devised for the protection of brass weights (J. J. Manley, *Phil. Mag.*, 1922, [vi], **44**, 948) is interesting. The procedure is to cover the weight with a thin film of linseed oil and heat it until the weight assumes a golden tint. The protective film which is formed is tough and may be polished. In this case it would seem that the protection is due both to

the oil and to an oxide film.   In Chapter VII. mention was made of the use of oils and greases in increasing the protection afforded by sulphide and other films, which may have little intrinsic protective effect, being applied mainly for decorative purposes. It is natural that all these foreign substances adhere more firmly to metals which already have a coating of a relatively porous material than to a clean metallic surface which is non-absorbent.

Paints.

The painting of metals has an economic significance which is far deeper than the æsthetic value of the pigment.   A judiciously chosen film of paint, applied under the best conditions to suit the particular needs of the situation in which the structure is exposed, may lengthen the effective life of the metal many times.

An ordinary paint is complex, containing (*a*) a drying oil such as tung oil or linseed oil, which on exposure to the air dries to a gelatinous substance, thereby forming a more or less impervious film over the metal ; (*b*) a drier, generally an oxide of manganese, cobalt, or some other metal exhibiting different stages of oxidation, which catalyses the drying process of the oil ; (*c*) the pigment (red lead, lead chromate, barium sulphate, and ferric oxide, among numerous other coloured substances), which not only provides the colour and prevents the surface of the metal from being seen through the gelatinous film, but also serves to prevent the film from cracking on drying ; (*d*) a thinner, such as turpentine, the chief function of which is to permit the easy spreading of the paint.

The factors affecting the corrosion of metal protected by so complex a system are necessarily complicated, for, in addition to electrochemical considerations, the colloidal properties of the paint vehicle have also to be kept in mind.   The properties of the pigment itself must be considered also ; for some have oxidising properties and may render the iron passive, thus increasing the protection ; and even the shape of the particles of pigment has its effect in preventing the access of moisture

to the metal, plate-like particles causing any diffusing substance to take a circuitous path. The amount of thinner affects the permeability of the paint film after the thinner has evaporated. A large number of factors have to be considered, therefore, before the suitability of a given paint for a particular purpose can be determined. As U. R. Evans has pointed out (*J. Soc. Chem. Ind.*, 1930, **49**, 173T), "the practice of bestowing care on the analysis of the metal and leaving the mixing of the paint in unscientific hands is illogical and wasteful." A considerable amount of research in the paint industry has been directed at the improvement of the smoothness and gloss of the coating, whilst from the economic point of view it is far better to consider the protective value of the paint on the underlying material. Where this is metal, the problem can be brought to a successful issue only by a thorough understanding of the principles discussed in this book. More co-operation between chemists engaged in the paint industry and those experienced in problems of corrosion would probably have far-reaching beneficial results.

Continuity, Adherence and Impermeability of the Paint Film.

Pigments are normally non-conductors of electricity and take no active part in electrochemical corrosion, unless they consist wholly or partly of a powdered metal, such as zinc, aluminium, or "bronze," or when they contain graphite. As the dried gelatinous film of paint acts by excluding corrosive materials from the surface of the metal, it must be capable in the first instance of forming a uniformly continuous film over the surface and must not crack on drying. A good paint will fulfil these requirements, but the relatively soft film is easily scratched, so that in service a paint film can scarcely be expected to remain perfectly continuous for long. Exposed parts at scratches are not subject to the relatively violent anodic attack of similar areas which are adjacent to films of cathodic metals, such as copper or nickel.

The adherence of the film of paint to the metal is an important factor, depending not only on the paint, but also on the surface of the metal. For example, paint does not hold satisfactorily to zinc-coated sheets unless they have been weathered for some time, or roughened by etching with solutions of copper salts or dilute hydrochloric acid. For mechanical reasons a paint will usually adhere better to a rough than to a smooth surface. For this reason partly, it is often best first to apply a protective coating of oxide, phosphate, or other compound and then to cover with a coating of paint.

The advisability of leaving scale on iron and steel before painting is still unsettled. The laborious operation of completely removing the scale must be avoided unless absolutely essential. It is quite clear, however, that all *loose* scale must be removed, as it will sooner or later peel off, and with it the paint. The remaining scale, provided it is dry and adherent, is probably harmless, and J. N. Friend (*Carn. Schol. Mem.*, 1913, **5,** 8) recommends its presence as giving a better grip for the paint.

Osmotic pressure may in certain cases cause the local failure of a paint film, as suggested by F. E. Bartell and M. van Loo (*Ind. Eng. Chem.*, 1925, **17**, 925, 1051). Electrolytes below the hardened paint film, perhaps enclosed in corrosion products, may cause water to be driven through the film by osmotic pressure, resulting in an increase of volume, which causes blistering of the film.

An important function of the paint is to exclude moisture and thus to prevent the electrochemical processes which produce ordinary rusting. Water should not be present initially, therefore, and films of moisture on the metal due to rain or dew should be avoided by painting in favourable weather and at a suitable time of the day. When the metal is already corroded it is more likely to retain moisture at its surface. The dried paint film should be impermeable to moisture, and the value of this property will increase generally with the thickness of the film. The permeability will depend to a great

extent on the nature of the vehicle and may vary with the conditions of service, for the film must be regarded as a colloidal gel, tending to swell in some solvents or in solutions of various electrolytes. The swollen film is soft and is easily rubbed off, and it will be permeable to the solution in which swelling occurs. The principles of colloid chemistry provide scope for the choice of vehicles for paints which are to be exposed to liquids. The particles of pigment also have some influence on the permeability of the paint film ; plate-like particles become oriented in a plane parallel with the surface of the metal when applied by brushing, and the layering thus produced ensures greater mechanical strength, and also causes any diffusing material to follow a devious path through the gelatinous medium between the particles of pigment. In addition to being water-proofing the paint film should be also impermeable to anions, particularly when the structure has to be exposed to sea-water.

The penetration of water through films of paint has been measured by G. H. Stanley (*S. African J. Sci.*, 1928, **25,** 111) by determining the change in the electrical conductivity of the film of paint. In this method a painted plate of metal is made the electrode of an electrolytic cell. If the circuit is maintained for ten to fifteen minutes, paint which has been penetrated by water peels off, owing to the liberation of gaseous hydrogen between the layer of paint and the surface of the metal. Of the paints examined, none was really waterproof for long, and after stripping off the paint it was found that rusting had occurred to a greater or less extent in every case. A cellulose lacquer almost entirely prevented rusting.

Protective Effect of the Pigment.

Some pigments are also mild oxidising agents, and these have the opportunity of conferring extra protection on the underlying metals, especially in the case of iron, by producing a passive layer at the surface. Notable among these are red lead and certain chromate pigments. Red lead is an ideal

priming coat for iron, and there is little doubt that its recognised protective properties are to be ascribed to its passivating influence, but the mechanical properties of the red-lead layer are not good, and it is usual to cover this layer with a film of another paint chosen for its mechanical properties, such as ferric oxide or aluminium. Aluminium paint is excellent for this purpose, as the flat scales of metal form a hard, compact layer, which gives mechanical strength and has the usual resistance of aluminium to atmospheric influences. When aluminium paint is applied directly to iron without the intermediate layer of red lead, it is in electrical contact and on exposure the aluminium becomes the anode. The iron is thereby cathodically protected, but the layer of paint suffers. Thus, the successive application of red-lead and aluminium paints has a double advantage.

There are numerous " bronze " paints, which, although excellent in their legitimate use, may intensify corrosion when applied directly to iron which is exposed, for example, to chloride solutions. The particles of pigment are cathodic to iron. Zinc paint, on the other hand, gives a layer which is anodic and corrodes preferentially to iron, just as the zinc on a galvanised iron sheet does, and zinc paint is sometimes applied to iron for that purpose. An objection to graphite paints has sometimes been raised on the ground that the graphite acts cathodically to iron and stimulates corrosion.

According to H. Röhrig (*Korrosion und Metallschutz*, 1929, **5,** 85), paints containing zinc, iron, and barium pigments in the usual oil media form efficient protective films on aluminium and its alloys, but paints containing lead pigments accelerate corrosion, the aluminium causing the separation of metallic lead from the paint, which then sets up local cells, causing heavy pitting.

An interesting protective coating is given by " Subox," which consists of finely-divided lead suboxide suspended in linseed oil, and is applied by spraying. After the application, the coating undergoes a slow transformation, resulting in a

film of metallic lead, held firmly as a protective coat by the oxidised oil.

The Effect of Corrosion Products on the Paint Film.

Assuming the paint film to be somewhat porous and to have no value as a passivating agent, it will certainly retard corrosion to some extent by reducing the rate of diffusion of oxygen, water, and electrolytes to the underlying metal, but in time corrosion is bound to occur through the usual processes. The corrosive agents, having penetrated the colloidal film, produce rust at the metal surface under the layer of paint. This process of rusting involves a considerable increase of volume, tending to push the film of paint away from the surface of the metal, and unless the paint has an extraordinary elasticity, failure of the film is bound to result. On the other hand, where normal rusting has occurred without penetration of the film, through scratches or perforations in the layer of paint, rust may develop in the form of excrescences outside the paint and interfere very little with its adherence.

The paint is impaired by another, quite distinct effect of the corrosion products. It has already been shown that the formation of rust on iron is a secondary reaction, the initial products in the presence of a film of aqueous solutions of sodium salts, for example, being a ferrous salt at the anodic areas and sodium hydroxide at the cathodic areas. U. R. Evans (*Trans. Amer. Electrochem. Soc.*, 1929, **55,** 243) has shown that this cathodically produced alkali may have a very important influence on the paint film, as in many cases it causes the colloidal constituents to swell or become peptised. Consequently, even if contact with the metal is not destroyed by the action of the alkali, the film is rendered very soft and liable to peel on rubbing. Alkali tends to creep between the metal and the paint, and the area thus adversely affected may become large. The degree of " alkaline peeling " will depend on the conditions of exposure and on the colloidal properties of the paint vehicle.

Lacquers.

Lacquers are solutions of gummy or resinous materials in volatile solvents and are applied by dipping, spraying, or brushing. A wide variety is available for different types of work, coloured or otherwise. Silvered articles are generally finished with a colourless lacquer, whilst a gold lacquer is used for brass. Natural gums and resins form the essential constituent of a large number of lacquers, and many of these are used as a solution in alcohol. Others require amyl acetate as a solvent and are not infrequently mixed with alcohol or benzene. Among these gums and resins may be mentioned shellac, copal, sandarac, mastic, and damar. A well-known lacquer is a solution of shellac in alcohol.

The pyroxylin lacquers contain derivatives of cellulose dissolved in amyl acetate, butyl acetate or other solvent, and have the advantage that metals so treated can be bent without cracking the film ; further, these lacquers do not become dull and opaque in time as do the resinous lacquers.

Whilst generally applied in the cold in the first instance, it is an advantage to harden lacquers by subsequent gentle heating in a stove. Reference to the lacquering of tinned food containers is made in Chapter VIII., page 213.

Enamels.

Vitreous enamels should not be confused with enamel paints, which are really paints to which varnish is added for the purpose of giving a high gloss. A vitreous enamel is a glassy composition, consisting in general of a borosilicate of sodium, potassium, calcium, and aluminium, and sometimes also lead, zinc, or barium. Other substances may be added in order to increase the strength or gloss, or to provide a particular colour. A high-quality white enamel is usually applied to iron over a ground coat, whilst coloured enamels are applied directly to the metal.

Enamels are frequently used to protect the metal work of stoves and other apparatus used for heating ; the expansion of the metal in relation to the base metal is an important matter.

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